

**APPENDIX H**

**STATISTICAL AND GEOCHEMICAL  
EVALUATIONS OF SITE METALS DATA**

## **STATISTICAL**

# **Statistical Comparison of Site and Background Data For CBR Proficiency Area (Parcel 517), Fort McClellan**

## **1.0 Introduction**

This report provides the Tier 1 and Tier 2 site-to-background comparison results for the CBR Proficiency Area (Parcel 517), Fort McClellan, in Calhoun County, Alabama. Tier 1 and Tier 2 evaluations have been performed on the soil and groundwater data sets. In the first step of the comparison, the maximum detected concentration (MDC) of each element is compared to two times the arithmetic mean of the background data (SAIC, 1998). Any metal that has an MDC greater than the background screening value is carried forward for Tier 2 evaluation, which includes the Slippage Test and the Wilcoxon Rank Sum Test (WRS).

The methodology and results of the Tier 1 and Tier 2 comparisons are summarized in Tables 1 through 3, and described in more detail in the following sections. Site samples used in the statistical site-to-background comparison include 7 surface soil samples (0 to 1 foot below ground surface [bgs]), 4 subsurface soil samples (2 to 8 feet bgs), and 4 groundwater samples that were collected at the site.

Background distributions and screening values have been established for target analyte list metals in surface soil, total soil (surface and subsurface soil combined), and groundwater for Fort McClellan (SAIC, 1998).

## **2.0 Comparison Methodology**

This section describes the statistical techniques that were employed in the CBR Proficiency Area (Parcel 517) site-to-background comparisons.

### **2.1 Statistical Procedures**

Contamination can be caused by a variety of processes that yield different spatial distributions of elevated contaminant concentrations. Slight but pervasive contamination can occur from non-point-source releases, and can result in slight increases in contaminant concentrations in a large percentage of samples. Localized, or “hot-spot,” contamination can result in elevated concentrations in a small percentage of the total number of site samples. No single two-sample statistical comparison test is sensitive to both of these modes of contamination. For this reason, the use of several simultaneous tests is recommended for a valid and complete comparison of site

Table 1

**Summary of Tier 1 and Tier 2 Site to Background Comparison  
Surface Soil, CBR Proficiency Area (Parcel 517)  
Fort McClellan  
Calhoun County, Alabama**

Metals	Frequency of Detection	Number of Detects Exceeding 2 X bkgd mean <sup>a</sup>	Slippage Test <sup>b</sup>	Wilcoxon Rank Sum Test <sup>b</sup>	Site MDC > Background 95th UTL/Percentile <sup>c</sup>	Carried Forward for Tier 3 Geochemical Evaluation
Aluminum	7 / 7	2	Pass	Fail	NA	Yes
Antimony	0 / 7	0	NA	NA	NA	
Arsenic	7 / 7	0	NA	NA	NA	
Barium	7 / 7	0	NA	NA	NA	
Beryllium	3 / 7	0	NA	NA	NA	
Cadmium	0 / 7	0	NA	NA	NA	
Calcium	7 / 7	3	Pass	Fail	NA	Yes
Chromium	7 / 7	0	NA	NA	NA	
Cobalt	7 / 7	0	NA	NA	NA	
Copper	7 / 7	4	Pass	Fail	NA	Yes
Iron	7 / 7	0	NA	NA	NA	
Lead	7 / 7	1	Pass	Fail	NA	Yes
Magnesium	7 / 7	3	Pass	Fail	NA	Yes
Manganese	7 / 7	0	NA	NA	NA	
Mercury	4 / 7	1	Pass	NA <sup>d</sup>	No	
Nickel	7 / 7	2	Pass	Fail	NA	Yes
Potassium	7 / 7	3	Pass	Fail	NA	Yes
Selenium	1 / 7	1	Pass	NA <sup>d</sup>	Yes	Yes
Silver	0 / 7	0	NA	NA	NA	
Sodium	7 / 7	0	NA	NA	NA	
Thallium	0 / 7	0	NA	NA	NA	
Vanadium	7 / 7	0	NA	NA	NA	
Zinc	7 / 7	5	Pass	Fail	NA	Yes

NA = not applicable; WRS =

a Tier 1 evaluation per **Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC: Revision 2**, Technical Memorandum, 24 June 2003 by Paul Goetchius.

b Part of Tier 2 evaluation per the above referenced memo.

c Performed within Tier 2 only when the Slippage test and/or WRS test cannot be performed.

d WRS test is not performed on data sets containing 50% or more nondetects.

Table 2

**Summary of Tier 1 and Tier 2 Site to Background Comparison**  
**Total Soil, CBR Proficiency Area (Parcel 517)**  
**Fort McClellan**  
**Calhoun County, Alabama**

Metals (mg/kg)	Frequency of Detection	Number of Detects Exceeding 2 X bkgd mean <sup>a</sup>	Slippage Test <sup>b</sup>	Wilcoxon Rank Sum Test <sup>b</sup>	Site MDC > Background 95th UTL/Percentile <sup>c</sup>	Carried Forward for Tier 3 Geochemical Evaluation
Aluminum	11 / 11	6	Passed	Failed	NA	Yes
Antimony	0 / 11	0	NA	NA	NA	
Arsenic	11 / 11	0	NA	NA	NA	
Barium	11 / 11	1	Passed	Failed	NA	Yes
Beryllium	6 / 11	2	Passed	Failed	NA	Yes
Cadmium	0 / 11	0	NA	NA	NA	
Calcium	9 / 11	4	Passed	Failed	NA	Yes
Chromium	11 / 11	0	NA	NA	NA	
Cobalt	11 / 11	1	Passed	Passed	NA	
Copper	11 / 11	5	Passed	Failed	NA	Yes
Iron	11 / 11	2	Passed	Passed	NA	
Lead	11 / 11	2	Passed	Failed	NA	Yes
Magnesium	11 / 11	7	Passed	Failed	NA	Yes
Manganese	11 / 11	0	NA	NA	NA	
Mercury	5 / 11	1	Passed	NA <sup>d</sup>	No	
Nickel	11 / 11	4	Passed	Failed	NA	Yes
Potassium	11 / 11	6	Passed	Failed	NA	Yes
Selenium	3 / 11	3	Passed	NA <sup>d</sup>	Yes	Yes
Silver	2 / 11	2	Passed	NA <sup>d</sup>	Yes	Yes
Sodium	11 / 11	0	NA	NA	NA	
Thallium	0 / 11	0	NA	NA	NA	
Vanadium	11 / 11	1	Passed	Passed	NA	
Zinc	11 / 11	7	Passed	Failed	NA	Yes

NA = not applicable

a Tier 1 evaluation per **Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC: Revision 2**, Technical Memorandum, 24 June 2003 by Paul Goetchius.

b Part of Tier 2 evaluation per the above referenced memo.

c Performed only when the Slippage test and/or WRS test cannot be performed.

d WRS test is not performed on data sets containing 50% or more nondetects.

Table 3

**Summary of Tier 1 and Tier 2 Site to Background Comparison**  
**Groundwater, CBR Proficiency Area, Parcel 517**  
**Fort McClellan**  
**Calhoun County, Alabama**

Metals	Frequency of Detection	Number of Detects Exceeding 2 X bkgd mean <sup>a</sup>	Slippage Test <sup>b</sup>	Wilcoxon Rank Sum Test <sup>b</sup>	Site MDC > Background 95th UTL/Percentile <sup>c</sup>	Carried Forward for Tier 3 Geochemical Evaluation
Aluminum	3 / 4	0	NA	NA	NA	
Antimony	0 / 4	0	NA	NA	NA	
Arsenic	4 / 4	0	NA	NA	NA	
Barium	4 / 4	0	NA	NA	NA	
Beryllium	0 / 4	0	NA	NA	NA	
Cadmium	0 / 4	0	NA	NA	NA	
Calcium	4 / 4	0	NA	NA	NA	
Chromium	0 / 4	0	NA	NA	NA	
Cobalt	1 / 4	0	NA	NA	NA	
Copper	0 / 4	0	NA	NA	NA	
Iron	4 / 4	0	NA	NA	NA	
Lead	0 / 4	0	NA	NA	NA	
Magnesium	4 / 4	2	Passed	NA <sup>e</sup>	Yes	Yes
Manganese	4 / 4	3	Passed	NA <sup>e</sup>	No	
Mercury	0 / 4	0	NA	NA	NA	
Nickel	1 / 4	1	NA <sup>d</sup>	NA <sup>e</sup>	No	
Potassium	4 / 4	0	NA	NA	NA	
Selenium	0 / 4	0	NA	NA	NA	
Silver	0 / 4	0	NA	NA	NA	
Sodium	0 / 4	0	NA	NA	NA	
Thallium	0 / 4	0	NA	NA	NA	
Vanadium	0 / 4	0	NA	NA	NA	
Zinc	0 / 4	0	NA	NA	NA	

NA = not applicable

a Tier 1 evaluation per **Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC: Revision 2**, Technical Memorandum, 24 June 2003 by Paul Goetchius.

b Part of Tier 2 evaluation per the above referenced memo.

c Performed only when the Slippage test and/or WRS test cannot be performed.

d Slippage test is not performed on data sets for which the maximum background value is a nondetect.

e WRS test is not performed when sample size is less than 5.

versus background distributions (U.S. Environmental Protection Agency [EPA], 1989, 1992, and 1994; U.S. Navy, 2002).

Analytes that fail the Tier 1 and Tier 2 comparisons are subject to a geochemical evaluation to determine if the elevated concentrations are due to natural processes or if they represent potential contamination.

### **2.1.1 Tier 1**

In this step of the background screening process, MDC of the site data set is compared to the background screening value of two times the background mean (SAIC, 1998). Elements for which the site MDC does not exceed the background screening value are considered to be present at background concentrations, and are not considered site-related chemicals. Elements for which the site MDC exceeds the background screening value undergo further evaluation (Tier 2).

### **2.1.2 Tier 2**

**Slippage Test.** The nonparametric Slippage test is designed to detect a difference between the upper tails of two distributions, and has been recommended for use in site-to-background comparisons to identify potential localized, or hot-spot, contamination (U.S. Navy, 2002). The test is performed by counting the number ( $K$ ) of detected concentrations in the site data set that exceed the maximum background measurement, and then comparing this number to a critical value ( $K_c$ ), which is a function of the number of background samples and the number of site samples. If  $K > K_c$ , then potential contamination is indicated and the analyte will be subjected to geochemical evaluation. If  $K \leq K_c$ , then localized contamination is not suspected.

Critical values tables for site and background data sets up to size  $n = 50$  are provided in U.S. Navy (2002). Critical values for larger data sets are calculated using the test statistic provided in Rosenbaum (1954). In this report, the Slippage test is performed at the 95 percent confidence level. The test cannot be performed if the maximum background value is a nondetect, because the actual concentration in that sample is unknown.

**Wilcoxon Rank Sum Test.** The nonparametric WRS test is designed to detect a difference between the medians of two data sets, and has been recommended for use in site-to-background comparisons to identify slight but pervasive contamination (EPA, 2000; U.S. Navy, 2002). In this report, the WRS test is performed when the site and background data sets each contain less than 50 percent nondetects (i.e., measurements reported as not detected below the laboratory

reporting limit). The WRS test will not be performed on data sets containing 50 percent or more nondetects. The medians of such data sets are unknown, and hence the test results would lack sufficient power to yield reliable results.

The WRS test compares two data sets of size  $n$  and  $m$  ( $n > m$ ), and tests the null hypothesis that the samples were drawn from populations with distributions having the same medians. To perform the test, the two sets of observations are pooled and arranged in order from smallest to largest. Each observation is assigned a rank; that is, the smallest is ranked 1, the next largest is ranked 2, and so on up to the largest observation, which is ranked  $(n + m)$ . If ties occur between or within samples, each one is assigned the mid-rank. Next, the sum of the ranks of smaller data set  $m$  is calculated. Then the test statistic  $Z$  is determined,

$$Z = \frac{W - m(m + n + 1)/2}{\sqrt{mn(m + n + 1)/12}}$$

Where:

- $W$  = Sum of the ranks of the smaller data set
- $m$  = Number of data points in smaller group
- $n$  = Number of data points in larger group.

This test statistic  $Z$  is used to find the two-sided significance. For instance, if the test statistic yields a probability of a Type I error (p-level) less than 0.2, then there is a statistically significant difference between the medians at the 80 percent confidence level. A Type I error involves rejecting the null hypothesis when it is true. If the p-level is greater than 0.2, then there is no reasonable justification to reject the null hypothesis at the 80 percent confidence level. It can therefore be concluded that the medians of the two data sets are similar, and it can be assumed to be drawn from the same population.

If the p-level is less than 0.2, then the medians of the two distributions are significantly different at the 80 percent confidence level. This can occur if the site data are shifted higher or lower than the background data. If the site data are shifted higher relative to background, then contamination may be indicated, and the analyte in question will be carried on for geochemical evaluation; however, if the site data are shifted lower relative to background, then contamination is not indicated. If the p-level is greater than 0.2, then pervasive site contamination is not suspected.



**Box Plots.** A quick, robust graphical method recommended by the EPA to visualize and compare two or more groups of data is the box plot comparison (EPA, 1989 and 1992). These plots provide a summary view of the entire data set, including the overall location and degree of symmetry. The box encloses the central 50 percent of the data points so that the top of the box represents the 75<sup>th</sup> percentile and the bottom of the box represents the 25<sup>th</sup> percentile. The small box within the larger box represents the median of the data set. The upper whisker extends outward from the box to the maximum point and the lower whisker extends to the minimum point. Nondetect results are set equal to one-half of the reporting limit for plotting purposes.

For each analyte, box plots of site and background data are placed side by side to visually compare the distributions and qualitatively determine whether the data sets are similar or distinct. Accordingly, the box plots are a necessary adjunct to the WRS test. As described previously, the WRS test may indicate that the medians of the site and background data sets are significantly different. Examination of the box plots will confirm whether that difference is caused by site data that are shifted higher or lower relative to background.

**Hot Measurement Test.** The hot measurement test consists of comparing each site measurement with a concentration value that is representative of the upper limit of the background distribution (EPA, 1994). Ideally, a site sample with a concentration above the background screening value would have a low probability of being a member of the background distribution, and may be an indicator of contamination. It is important to select such a background screening value carefully so that the probability of falsely identifying site samples as contaminated or uncontaminated is minimized.

The 95<sup>th</sup> upper tolerance limit (95<sup>th</sup> UTL) is recommended as a screening value for normally or lognormally distributed analytes and the 95<sup>th</sup> percentile is recommended as a screening value for nonparametrically distributed analytes (EPA, 1989, 1992, and 1994). Site samples with concentrations above these values are not necessarily contaminated, but should be considered suspect. To perform the test, each analyte's site MDC is compared to the background 95<sup>th</sup> UTL or 95<sup>th</sup> percentile, in accordance with the type of background distribution. If the site MDC exceeds the background screening value, then that analyte will undergo a geochemical evaluation. If the MDC does not exceed the background threshold value, then hot-spot contamination is not indicated.

### **2.1.3 Geochemical Evaluation**

If an analyte fails either of the statistical tests described above, then a geochemical evaluation is performed to determine if the elevated concentrations are caused by natural processes. The methodology and results of the geochemical evaluation are provided separately in this appendix.

## **3.0 Results of the Site-to-Background Comparisons**

This section presents the results of the site-to-background comparisons for 23 metals in the CBR Proficiency Area (Parcel 517) soil and groundwater samples. Soil is evaluated as surface soil (0 to 1 foot bgs) and total soil (surface and subsurface soil (0-8 feet bgs) combined). Statistical test results are discussed in detail below for each metal evaluated. Box plots are discussed and provided in Attachment 1 of this report. Tables 1 through 3 summarize the Tier 1 and Tier 2 test results for each media as discussed in the following sections.

### **3.1 Surface Soil**

Twenty-three TAL metals were evaluated in the CBR Proficiency Area (Parcel 517) surface soil. Antimony, cadmium, silver, and thallium had no detects in the surface soil site samples, so no further discussion of these metals is included. Nine metals (arsenic, barium, beryllium, chromium, cobalt, iron, manganese, sodium, and vanadium) were eliminated in the Tier 1 evaluation and will not be discussed any further.

The metals carried forward for Tier 2 evaluation, (aluminum calcium, copper, lead, magnesium, mercury, nickel, potassium, selenium, and zinc), have the Slippage test and WRS test performed. The results of the Tier 2 evaluation are discussed below in detail. Box plots are provided in Attachment 1.

Table 1 summarizes the surface soil Tier 1 and Tier 2 evaluation.

#### **Aluminum**

##### Tier 1 Evaluation

Two site samples exceed the background screening value of 1.6E+4 milligrams per kilogram (mg/kg).

##### Slippage Test

The critical value,  $K_c$ , is 2. There were no site samples exceeding the maximum background measurement ( $K=0$ ). Because  $K < K_c$ , aluminum passes the Slippage Test.

#### WRS Test

The WRS test p-level of 7.4E-3 indicates significant difference between the site and background distributions.

#### Box Plot

Box plots for the site and background data sets are provided in Figure 1-1. The site minimum and interquartile range are higher than the corresponding background values.

#### Conclusion

Because aluminum in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

### **Calcium**

#### Tier 1 Evaluation

Three site samples exceed the background screening value of 1.7E+3 mg/kg.

#### Slippage Test

$K_c$  for calcium is two and no site samples exceed the maximum background measurement. Because  $K < K_c$  calcium passes the Slippage Test.

#### WRS Test

The p-level of 0.013 indicates a significant difference between the site and background distributions.

#### Box Plot

The site minimum and interquartile range are higher than their respective background values (Figure 1-1).

#### Conclusion

Because calcium in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

### **Copper**

#### Tier 1 Evaluation

Copper has four site samples exceeding the background screening value of 1.3E+1 mg/kg.

#### Slippage Test

$K_c$  of copper is two, and two site samples exceed the maximum background measurement. Because  $K \leq K_c$  copper passes the Slippage test.

#### WRS Test

The p-level of 0.0035 indicates a significant difference between the site and background distributions.

### Box Plot

The site minimum, interquartile range, and maximum are higher than the corresponding background values (Figure 1-2).

### Conclusion

Because copper in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

## **Lead**

### Tier 1 Evaluation

One site sample exceeds the background screening value of  $4.0E+1$  mg/kg.

### Slippage Test

$K_c$  for lead is two, and there are no detects in the site samples exceeding the maximum background measurement. Because  $K < K_c$ , lead passes the Slippage Test.

### WRS Test

The p-level of  $1.7E-1$  indicates a very slight difference between the site and background distributions.

### Box Plot

The site minimum and interquartile range are higher than the corresponding background, and the site maximum is lower than background (Figure 1-2).

### Conclusion

Because lead in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

## **Magnesium**

### Tier 1 Evaluation

Three site samples exceed the background screening value of  $1.0E+3$  mg/kg.

### Slippage Test

$K_c$  for magnesium is two, and no detects in the site samples exceed the maximum background measurement. Because  $K < K_c$ , magnesium passes the Slippage Test.

### WRS Test

The p-level of  $< 0.001$  indicates significant difference between the site and background distributions.

### Box Plot

The site minimum and interquartile range are elevated with respect to background (Figure 1-3).

### Conclusion

Because magnesium in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

## **Mercury**

### Tier 1 Evaluation

One of the detected concentrations exceeds the background screening value of  $8.0\text{E-}2$  mg/kg.

### Slippage Test

$K_c$  for mercury is two, and no detects in site samples exceed the maximum background measurement. Since  $K < K_c$ , mercury passes the Slippage test.

### WRS Test

The WRS test was not performed because the background data sets contains  $< 50$  percent detects.

### Hot Measurement Test

No samples exceed the background 95<sup>th</sup> percentile of 0.125 mg/kg.

### Box Plot

The site minimum and interquartile range appear slightly elevated with respect to background (Figure 1-3).

### Conclusion

Because the background 95<sup>th</sup> percentile is greater than the site MDC, mercury is considered to be within the range of background.

## **Nickel**

### Tier 1 Evaluation

Two of the detected concentrations of nickel in site samples exceed the background screening value of  $1.0\text{E+}1$  mg/kg.

### Slippage Test

$K_c$  for nickel is 2, and no detects in site samples exceed the maximum background measurement. Because  $K < K_c$ , nickel passes the Slippage Test.

### WRS Test

The p-level of  $7.6\text{E-}3$  indicates a significant difference between the site and background distributions.

### Box Plot

The site minimum and interquartile range are higher compared with the corresponding background values (Figure 1-4). The site maximum is lower than that of background.

### Conclusion

Because nickel in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

## **Potassium**

### Tier 1 Evaluation

Three site samples exceed the background screening value of 800 mg/kg.

### Slippage Test

$K_c$  for potassium is 2, and there are no detects in site samples that exceed the maximum background measurement. Because  $K < K_c$  potassium passes the Slippage Test.

### WRS Test

The p-level of  $< 0.001$  indicates a significant difference between the site and background distributions.

### Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-4). The site maximum is significantly less than the background maximum.

### Conclusion

Because potassium in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

## **Selenium**

### Tier 1 Evaluation

One detected concentration in the site data set exceeds the background screening value of 0.48 mg/kg.

### Slippage Test

$K_c$  for selenium is 2, and no site samples exceed the maximum background measurement. Because  $K < K_c$ , selenium passes the Slippage test.

### WRS Test

No WRS test was performed because the site and background data sets each contain  $> 50$  percent nondetects.

### Hot Measurement Test

One site sample exceeds the background 95<sup>th</sup> percentile of 0.563 mg/kg.

### Box Plot

The shape and location of the site and background box plot are defined by the high percentage of nondetects (14% and 11% respectively), and the replacement values of one-half the reporting limit (Figure 1-5).

### Conclusion

Because selenium in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

## **Zinc**

### Tier 1 Evaluation

Five site samples exceed the background screening value of 41 mg/kg.

### Slippage Test

$K_c$  for zinc is 2, and there are no detects in site samples exceeding the maximum background measurement. Because  $K < K_c$ , zinc passes the Slippage Test.

### WRS Test

The p-level of  $< 0.001$  indicates significant difference between the site and background distributions.

### Box Plot

The site minimum and interquartile range are slightly higher than their respective background values (Figure 1-5).

### Conclusion

Because zinc in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

## **3.2 Total Soil**

Twenty-three TAL metals were evaluated in the CBR Proficiency Area (Parcel 517) total soil. Antimony, cadmium, and thallium had no detected concentrations in the total soil site samples, so no further discussion of these metals is included. Arsenic, chromium, manganese, and sodium were eliminated in the Tier 1 evaluation and will not be discussed any further. The remaining sixteen metals are carried forward for Tier 2 evaluation. The statistical test results are summarized in Table 3 and discussed in detail below. The box plots are provided in Attachment 1.

## **Aluminum**

### Tier 1 Evaluation

Six site samples exceed the background screening value of  $1.5E+4$  milligrams per kilogram (mg/kg).

### Slippage Test

$K_c$  for aluminum is two, and there were no site samples exceeding the maximum background measurement. Because  $K < K_c$ , aluminum passes the Slippage test.

### WRS Test

The WRS test p-level of  $< 0.001$  indicates significant difference between the site and background distributions.

### Box Plot

Box plots for the site and background data sets are provided in Figure 1-6. The site minimum and interquartile range are higher than the corresponding background values.

### Conclusion

Because aluminum in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

## **Barium**

### Tier 1 Evaluation

One site sample exceeds the background screening value of  $1.8E+2$  mg/kg.

### Slippage Test

$K_c$  for barium is 2 and no site samples exceed the maximum background measurement. Because  $K < K_c$  barium passes the Slippage Test.

### WRS Test

The p-level of 0.0034 indicates a difference between the site and background distributions.

### Box Plot

The site minimum and interquartile range are slightly different than their respective background values (Figure 1-6). The site maximum is lower than that of background.

### Conclusion

Because barium in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

## **Beryllium**

### Tier 1 Evaluation

Beryllium has two site samples exceeding the background screening value of  $8.3E-1$ .

### Slippage Test

$K_c$  of beryllium is two, and no site samples exceed the maximum background measurement. Because  $K < K_c$  beryllium passes the Slippage test.

### WRS Test

The p-level of  $5.4E-4$  indicates a significant difference between the site and background distributions.

### Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-7). The site maximum is lower than that of background.

### Conclusion

Because beryllium in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.



## **Calcium**

### Tier 1 Evaluation

Four site samples exceed the background screening value of  $1.2\text{E}+3$  mg/kg.

### Slippage Test

$K_c$  for calcium is 2 and no site samples exceed the maximum background measurement.

Because  $K < K_c$ , calcium passes the Slippage Test.

### WRS Test

The p-level of 0.04 indicates a significant difference between the site and background distributions.

### Box Plot

The site minimum and the interquartile range are elevated with respect to the corresponding background values (Figure 1-7).

### Conclusion

Because calcium in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

## **Cobalt**

### Tier 1 Evaluation

Cobalt has one site sample exceeding the background screening value of  $1.6\text{E}+1$ .

### Slippage Test

$K_c$  of cobalt is two, and no site samples exceed the maximum background measurement.

Because  $K < K_c$  copper passes the Slippage test.

### WRS Test

The p-level of 0.59 indicates strong agreement between site and background distributions.

### Box Plot

The site minimum and interquartile range are similar to that of background (Figure 1-8). The site maximum is significantly lower than the corresponding background values.

### Conclusion

Cobalt is considered within the range of background.

## **Copper**

### Tier 1 Evaluation

Copper has five site samples exceeding the background screening value of  $1.6\text{E}+1$ .

### Slippage Test

$K_c$  of copper is two, and no site samples exceed the maximum background measurement.

Because  $K < K_c$ , copper passes the Slippage test.

#### WRS Test

The p-level of  $< 0.001$  indicates a significant difference between the site and background distributions.

#### Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-8).

#### Conclusion

Because copper in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

### **Iron**

#### Tier 1 Evaluation

Two site samples exceed the background screening value of  $3.9E+4$  mg/kg.

#### Slippage Test

$K_c$  for iron is two, and there are no detects in the site samples exceeding the maximum background measurement. Because  $K < K_c$ , iron passes the Slippage Test.

#### WRS Test

The p-level of 0.23 indicates good agreement between site and background distributions.

#### Box Plot

The site minimum and interquartile range are just slightly elevated compared to the corresponding background values (Figure 1-9). The site maximum is lower than that of background.

#### Conclusion

Because iron in total soil failed statistical comparison to background, it is considered within the range of background.

### **Lead**

#### Tier 1 Evaluation

Two site samples exceed the background screening value of 39 mg/kg.

#### Slippage Test

$K_c$  for lead is two, and there are no detects in the site samples exceeding the maximum background measurement. Because  $K < K_c$ , lead passes the Slippage test.

#### WRS Test

The p-level of 0.04 indicates a significant difference between the site and background distributions.

#### Box Plot

The site minimum and interquartile range are higher than the corresponding background, and the site maximum is significantly lower than background (Figure 1-9).

#### Conclusion

Because lead in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

### **Magnesium**

#### Tier 1 Evaluation

Seven site samples exceed the background screening value of 910 mg/kg.

#### Slippage Test

$K_c$  for magnesium is 2, and no detects in the site samples exceed the maximum background measurement. Because  $K < K_c$ , magnesium passes the Slippage Test.

#### WRS Test

The p-level of  $< 0.001$  indicates significant difference between the site and background distributions.

#### Box Plot

The site minimum and interquartile range are elevated with respect to background (Figure 1-10).

#### Conclusion

Because magnesium in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

### **Mercury**

#### Tier 1 Evaluation

One of the detected concentrations exceeds the background screening value of  $7.0E-2$  mg/kg.

#### Slippage Test

$K_c$  for mercury is 2, and no detects in site samples exceed the maximum background measurement. Since  $K < K_c$ , mercury passes the Slippage Test.

#### WRS Test

The WRS test was not performed because the site and background data sets contain  $< 50$  percent detects.

#### Box Plot

The site minimum and interquartile range are higher compared to the corresponding background values (Figure 1-10).

#### Hot Measurement Test

No samples exceed the background 95<sup>th</sup> percentile of 0.094 mg/kg.

### Conclusion

Mercury is considered within the range of background.

## **Nickel**

### Tier 1 Evaluation

Four of the detected concentrations of nickel in site samples exceed the background screening value of 12 mg/kg.

### Slippage Test

$K_c$  for nickel is 2, and no detects in site samples exceed the maximum background measurement. Because  $K < K_c$ , nickel passes the Slippage test.

### WRS Test

The p-level of  $< 0.001$  indicates a significant difference between the site and background distributions.

### Box Plot

The site minimum and interquartile range are higher compared with the corresponding background values (Figure 1-11).

### Conclusion

Because nickel in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

## **Potassium**

### Tier 1 Evaluation

Six site samples exceed the background screening value of 760 mg/kg.

### Slippage Test

$K_c$  for potassium is 2, and there are no detects in site samples that exceed the maximum background measurement. Because  $K < K_c$  potassium passes the Slippage Test.

### WRS Test

The p-level of  $< 0.001$  indicates a significant difference between the site and background distributions.

### Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-11).

### Conclusion

Because potassium in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

## **Selenium**

### Tier 1 Evaluation

Three detected concentrations in the site data set exceed the background screening value of 4.8E-1 mg/kg.

### Slippage Test

$K_c$  for selenium is 2, and no site samples exceed the maximum background measurement. Because  $K < K_c$ , selenium passes the Slippage test.

### WRS Test

No WRS test was performed because the site and background data sets each contain <50 percent detects.

### Box Plot

The shape and location of the background and site box plots are defined by the high percentage of nondetects (73 and 98 percent respectively), and the replacement values of one-half the reporting limit (Figure 1-12).

### Hot Measurement Test

Three site samples exceed the 95<sup>th</sup> percentile of 0.571 mg/kg.

### Conclusion

Because selenium in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

## **Silver**

### Tier 1 Evaluation

Two detected concentrations in the site data set exceed the background screening value of 3.0E-1 mg/kg.

### Slippage Test

$K_c$  for silver is two, and no site samples exceed the maximum background measurement. Because  $K < K_c$ , silver passes the Slippage test.

### WRS Test

No WRS test was performed because the site data set contains <50 percent detects.

### Box Plot

The shape and location of the site box plots are defined by the high percentage of nondetects (82 percent), and the replacement values of one-half the reporting limit (Figure 1-12).

### Hot Measurement Test

Two site samples exceed the 95<sup>th</sup> percentile of 0.803 mg/kg.

### Conclusion

Because silver in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

## **Vanadium**

### Tier 1 Evaluation

One detected concentration in the site data set exceeds the background screening value of 6.2E+1 mg/kg.

### Slippage Test

$K_c$  for vanadium is two, and no site samples exceed the maximum background measurement. Because  $K < K_c$ , vanadium passes the Slippage test.

### WRS Test

The p-level of 0.2 indicates good agreement between the site and background distributions.

### Box Plot

The site minimum and 25<sup>th</sup> percentile are elevated as compared to that of background. The site median and 75<sup>th</sup> percentile are about the same as the corresponding background values, and the site maximum is lower than that of background (Figure 1-13).

### Conclusion

Vanadium is considered within the range of background.

## **Zinc**

### Tier 1 Evaluation

Seven site samples exceed the background screening value of 38 mg/kg.

### Slippage Test

$K_c$  for zinc is two, and there are no detects in site samples exceeding the maximum background measurement. Because  $K < K_c$ , zinc passes the Slippage Test.

### WRS Test

The p-level of <0.001 indicates significant difference between the site and background distributions.

### Box Plot

The site minimum and interquartile range are higher than their respective background values (Figure 1-13). The site maximum is lower than the corresponding background value.

### Conclusion

Because zinc in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

### **3.3 Groundwater**

This section presents the results of the site-to-background comparisons for 23 metals from unfiltered groundwater site samples. Thirteen of the metals (antimony, beryllium, cadmium, chromium, copper, lead, mercury, selenium, silver, sodium, thallium, vanadium, and zinc) had no detects in the site samples and are not considered any further. Another seven metals (aluminum, arsenic, barium, calcium, cobalt, iron, and potassium) had no detected concentrations that exceeded their respective background screening values. These metals are considered within the range of background based on the Tier 1 evaluation. Table 3 summarizes these results.

The remaining three metals (magnesium, manganese, and nickel) have detected concentrations exceeding the background screening value, and are carried forward for Tier 2 evaluation. The test results of the Tier 2 evaluation are discussed below in detail. Box plots are provided in Attachment 1.

#### **Magnesium**

##### Tier 1 Evaluation

Two of the detected concentrations exceed the background screening value of 21.3 mg/L.

##### Slippage Test

$K_c$  for magnesium is 2, and no detects in site samples exceed the maximum background measurement. Since  $K < K_c$ , magnesium passes the Slippage Test.

##### WRS Test

The WRS test cannot be performed when the site data has less than 5 samples.

##### Box Plot

The site minimum and interquartile range are higher compared to the corresponding background values (Figure 1-14).

##### Hot Measurement Test

One sample exceeds the background 95<sup>th</sup> percentile of 22 mg/L.

##### Conclusion

Because magnesium in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

#### **Manganese**

##### Tier 1 Evaluation

Three detected concentrations exceed the background screening value of 0.581 mg/L.

#### Slippage Test

$K_c$  is 2, and no detects in site samples exceed the maximum background measurement. Since  $K < K_c$ , manganese passes the Slippage test.

#### WRS Test

The WRS test cannot be performed when the site data has less than 5 samples.

#### Box Plot

The site minimum and interquartile range appear higher compared to the corresponding background values (Figure 1-14), and the site maximum is lower than that of background.

#### Hot Measurement Test

No samples exceed the background 95<sup>th</sup> percentile of 4.134 mg/L.

#### Conclusion

Based on the Slippage test and the Hot Measurement Test, manganese is considered within the range of background.

### **Nickel**

#### Tier 1 Evaluation

There is no background screening value available for nickel, and one site sample has a detected result.

#### Slippage Test

The Slippage test cannot be performed because the background maximum value is a nondetect.

#### WRS Test

The WRS test cannot be performed when the site data has less than 5 samples.

#### Box Plot

The site minimum and interquartile range are higher compared to the corresponding background values (Figure 1-15).

#### Hot Measurement Test

No samples exceed the background 95<sup>th</sup> percentile of 0.0343 mg/L.

#### Conclusion

Based on the Hot Measurement Test, nickel is considered within the range of background.

## **4.0 Summary and Conclusions**

The statistical methodology used to compare the CBR Proficiency Area (Parcel 517) and background data sets for 23 elements in soil and groundwater includes a comparison of the site MDC to the background screening value. Analytes that failed this comparison were subjected to the Slippage test and WRS test, and box-and-whisker plots were prepared to visually compare



the two data sets and properly interpret the WRS test results. Analytes that failed either the Slippage test or Wilcoxon rank sum test will be carried forward for Tier 3 geochemical evaluation to determine if natural processes can explain the elevated concentrations.

Tables 1 through 3 summarize the comparison test results and show the metals carried forward for geochemical evaluation.

## **5.0 References**

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U.S. Navy, 2002, *Guidance for Environmental Background Analysis, Volume 1: Soil*, NFESC User's Guide UG-2049-ENV, Naval Facilities Engineering Command, Washington, D.C., April.

## **ATTACHMENT 1**

Figure 1-1

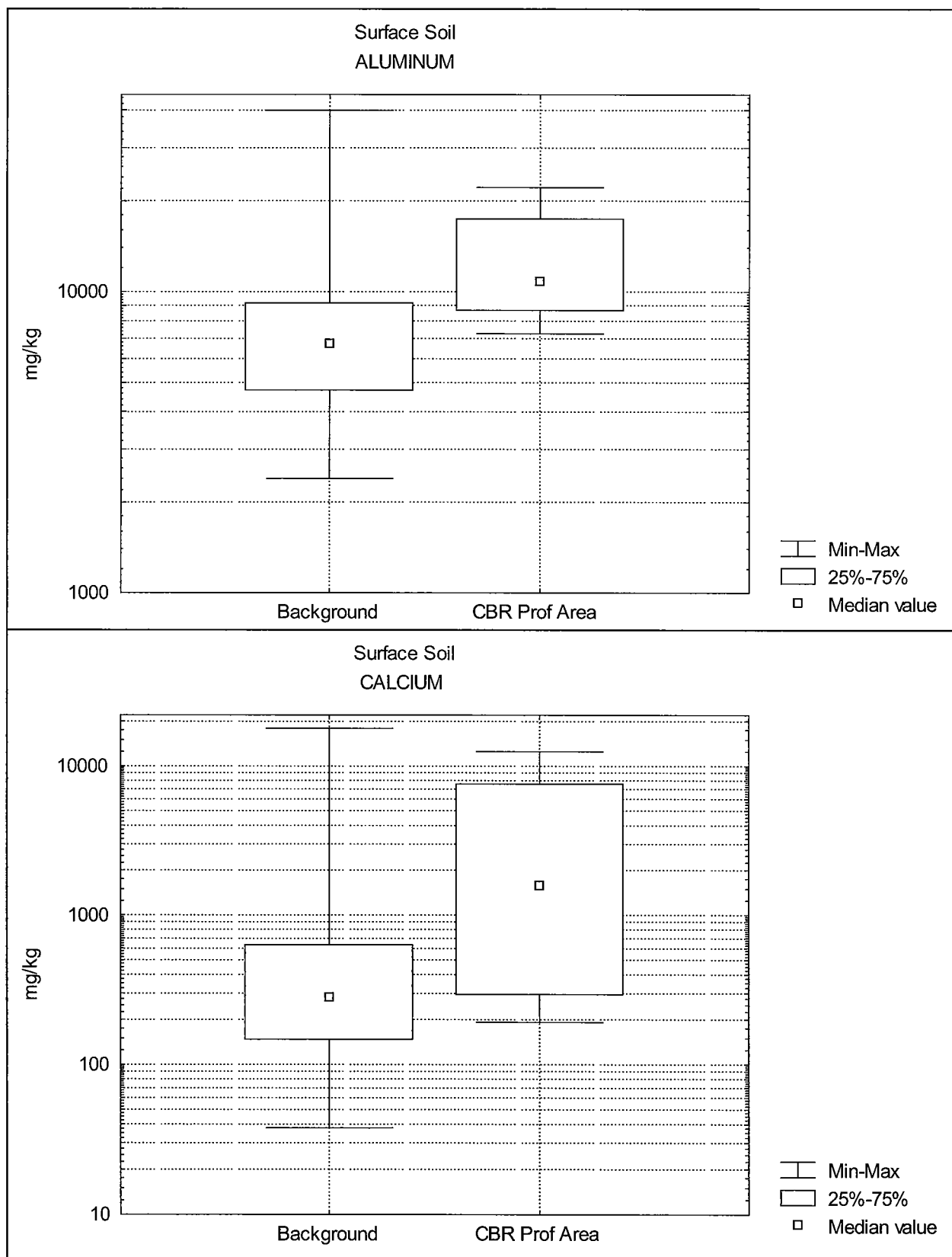


Figure 1-2

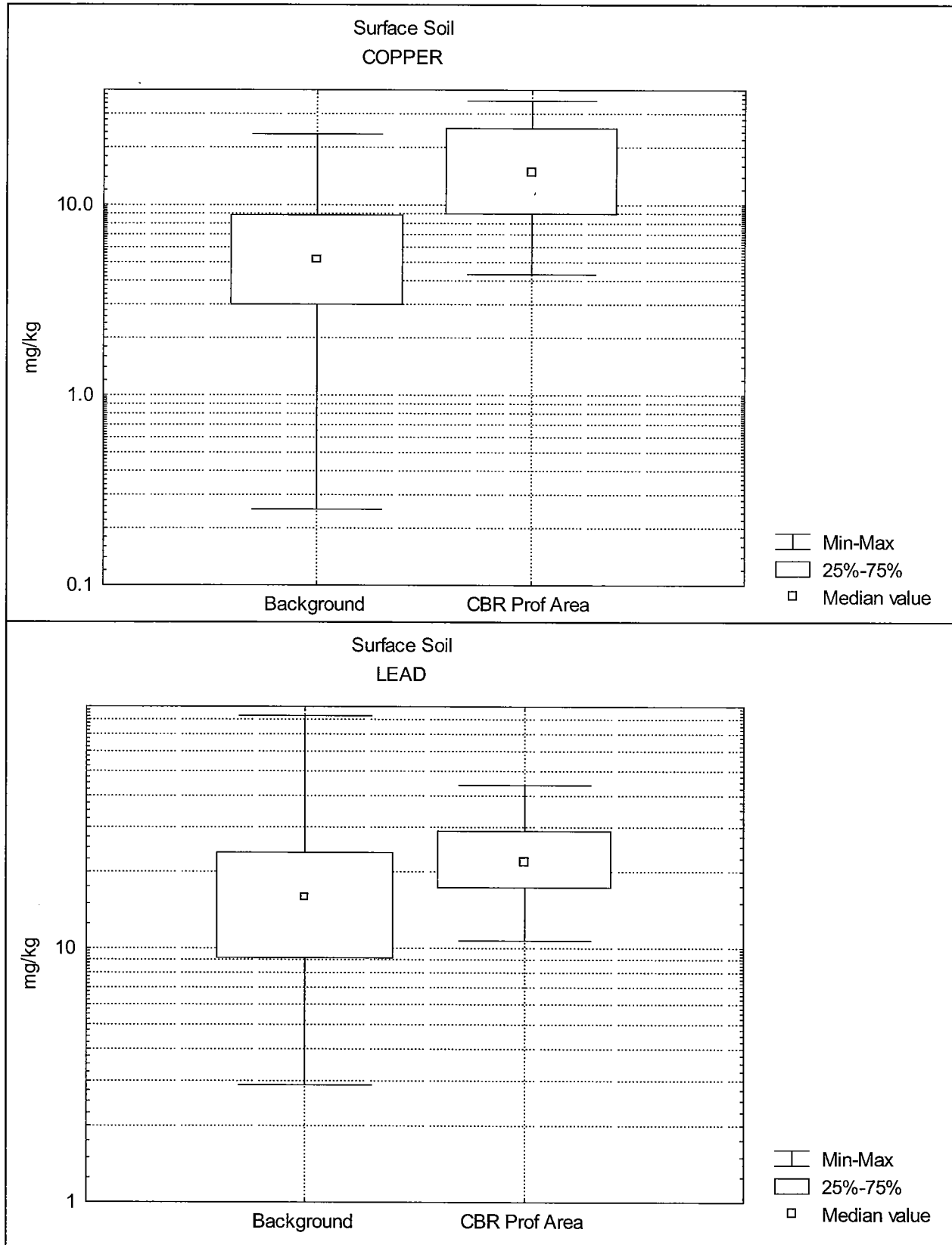


Figure 1-3

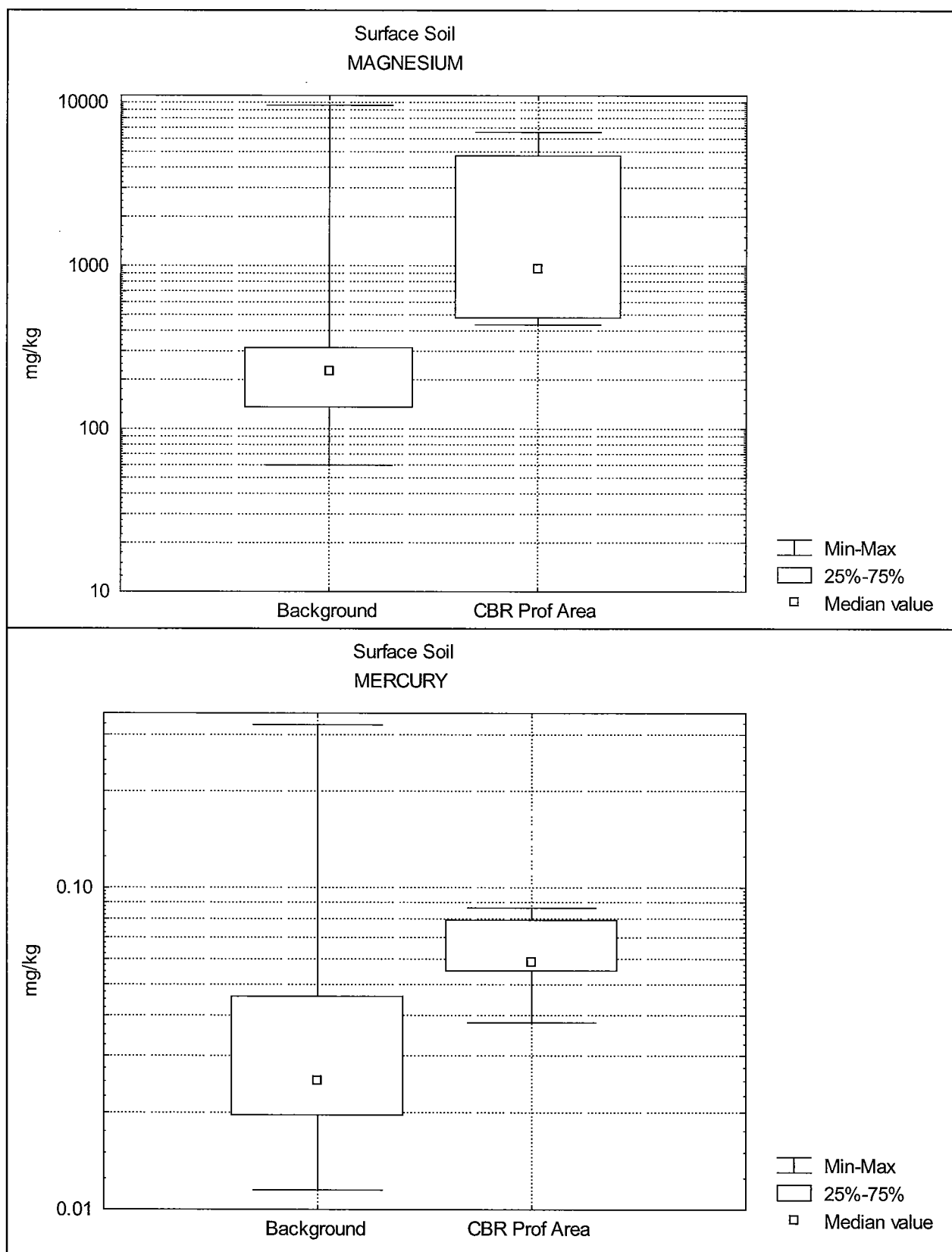


Figure 1-4

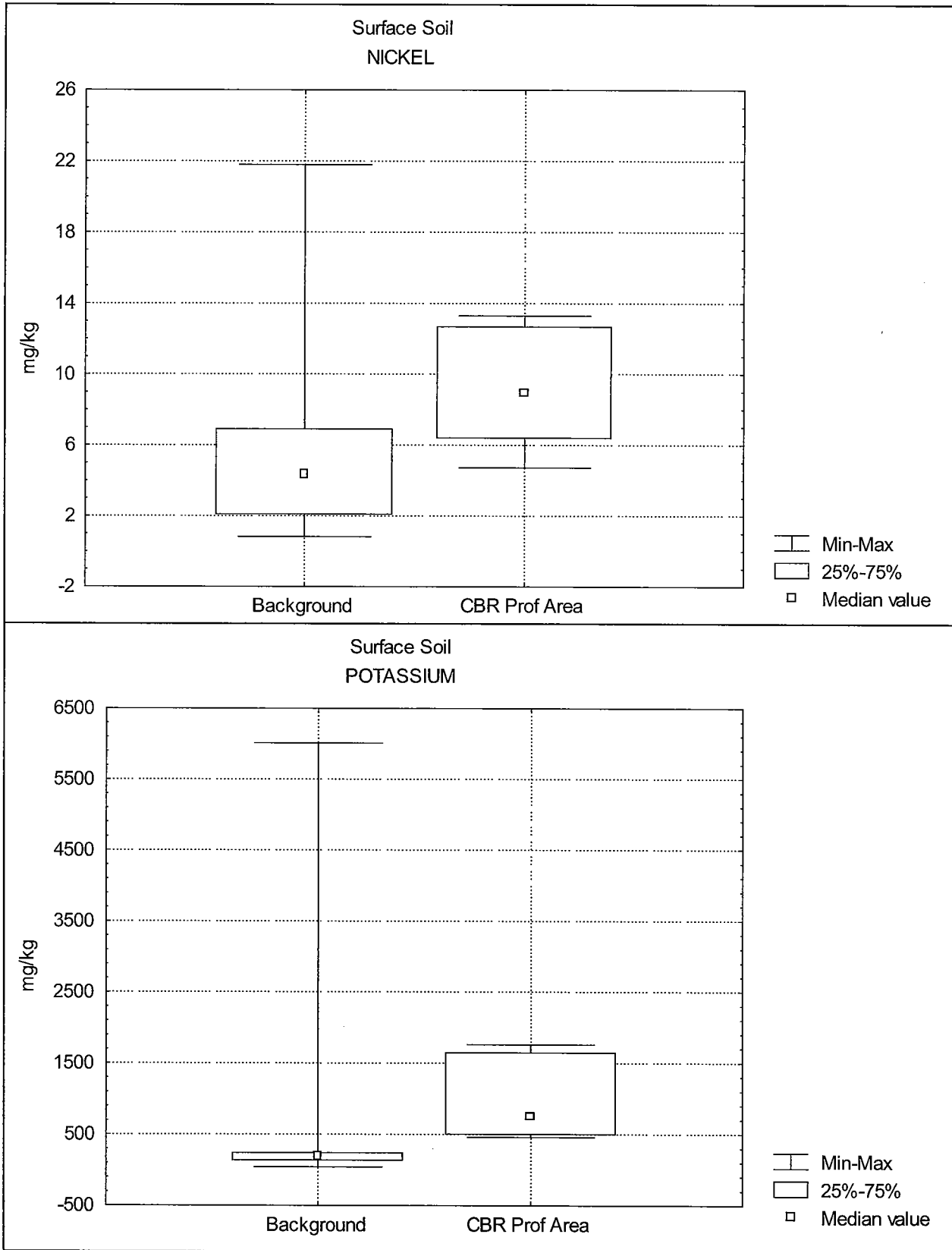


Figure 1-5

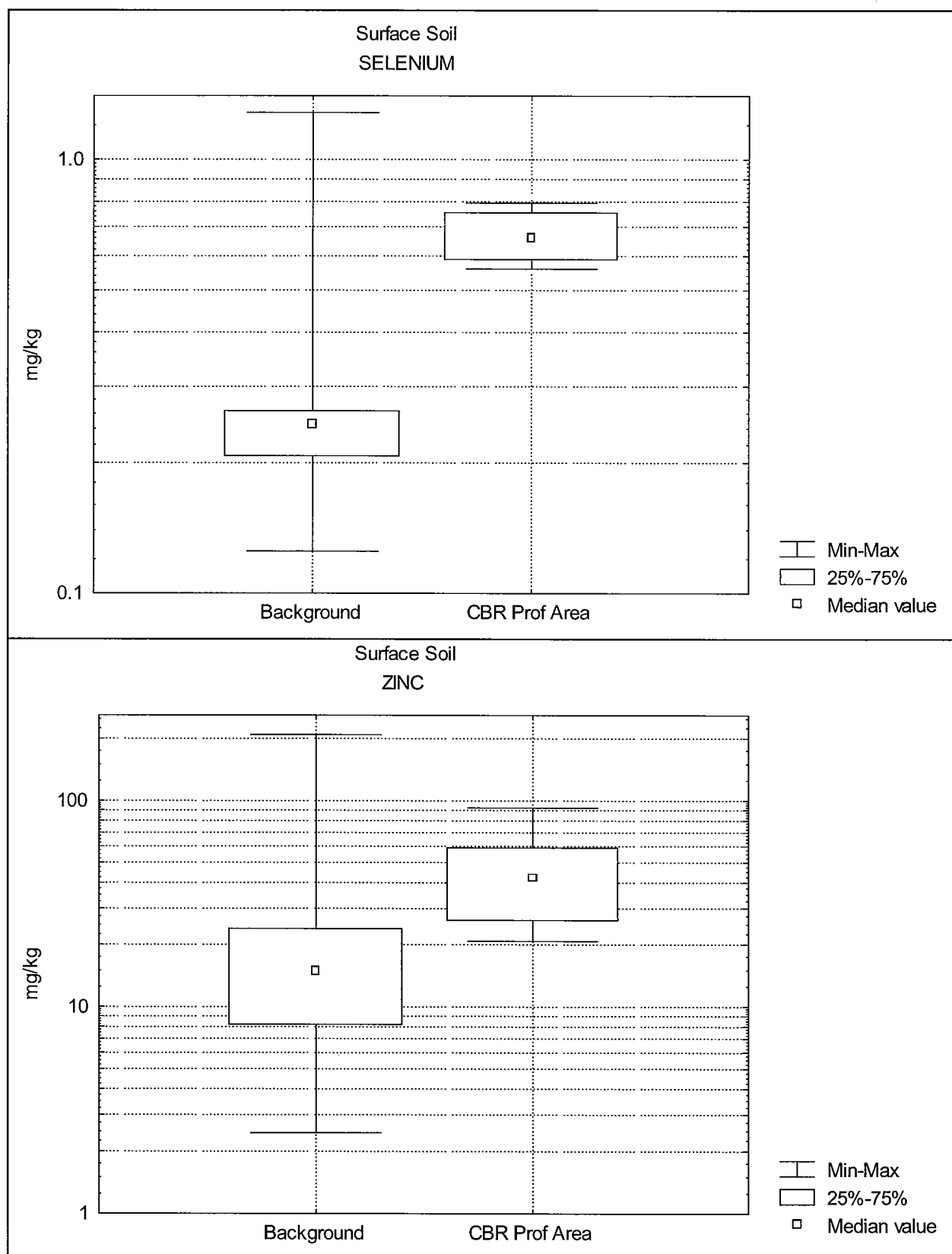


Figure 1-6

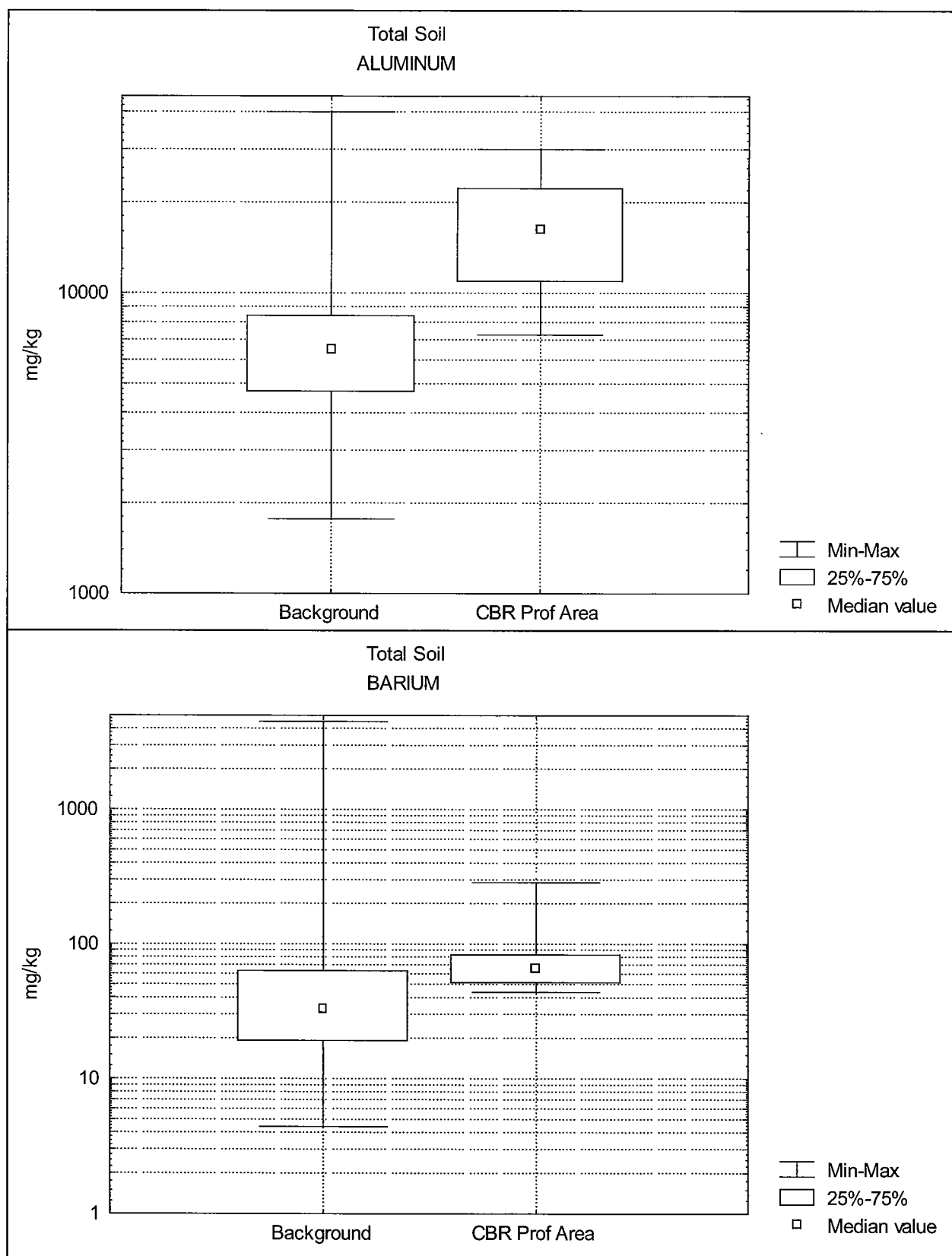




Figure 1-7

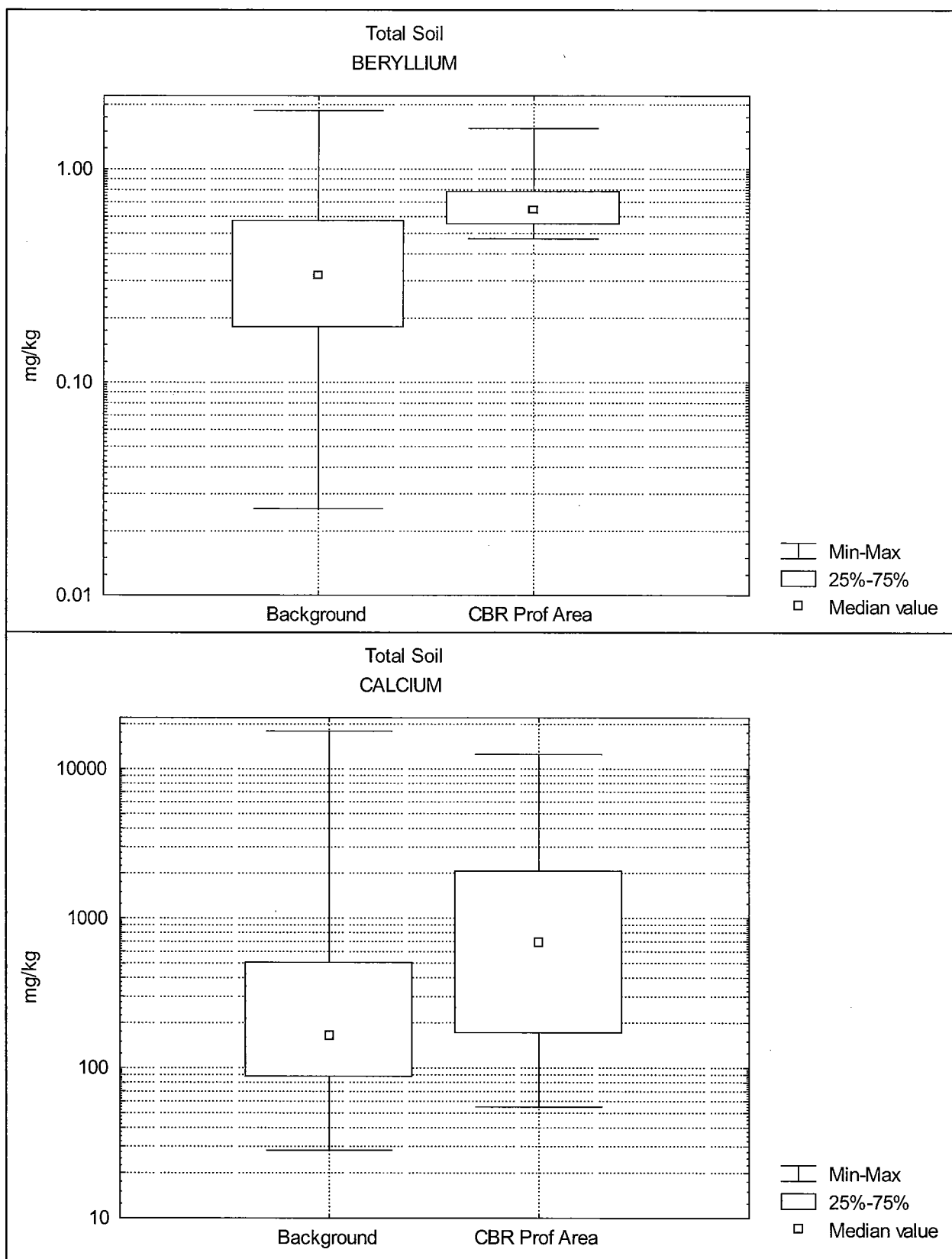


Figure 1-8

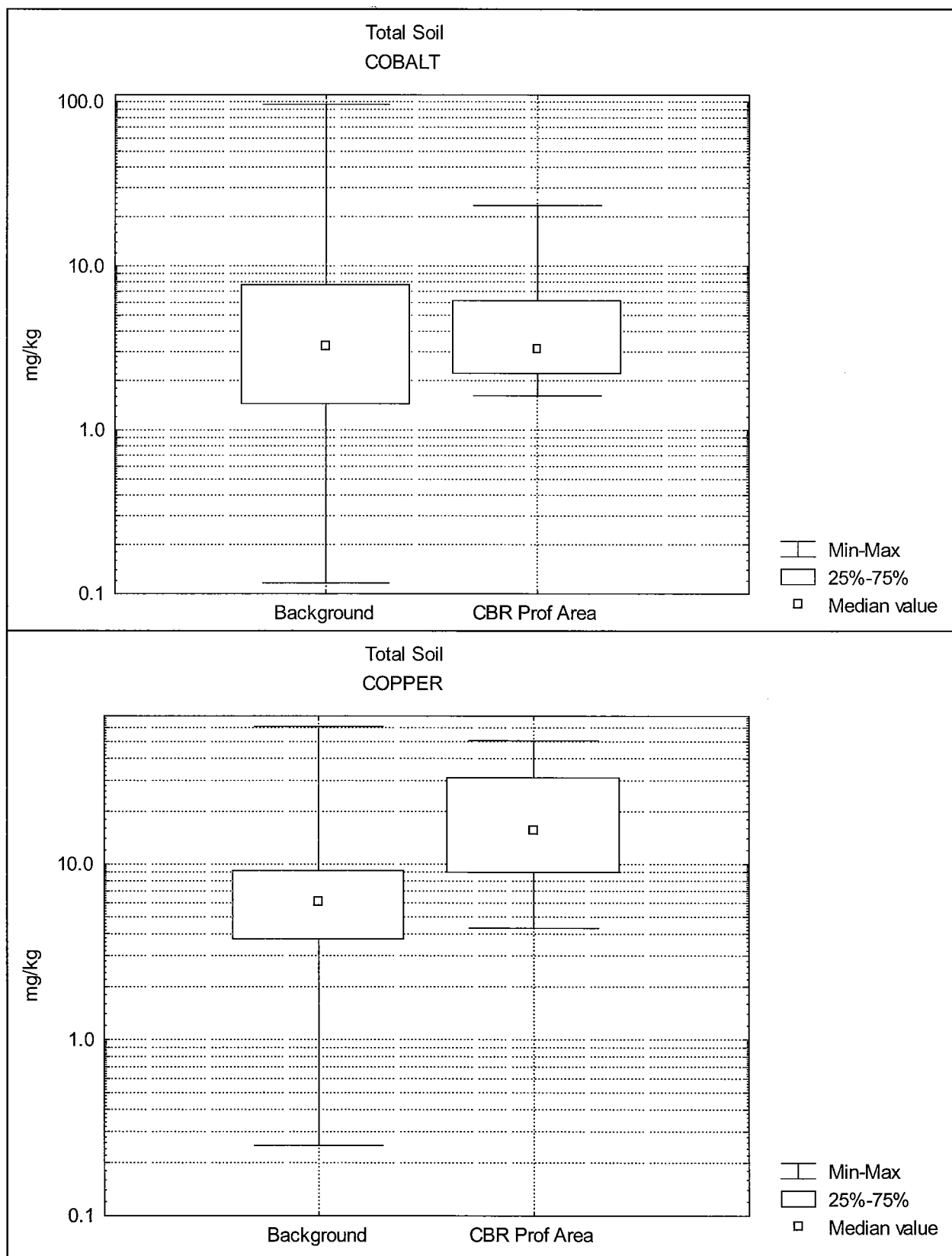


Figure 1-9

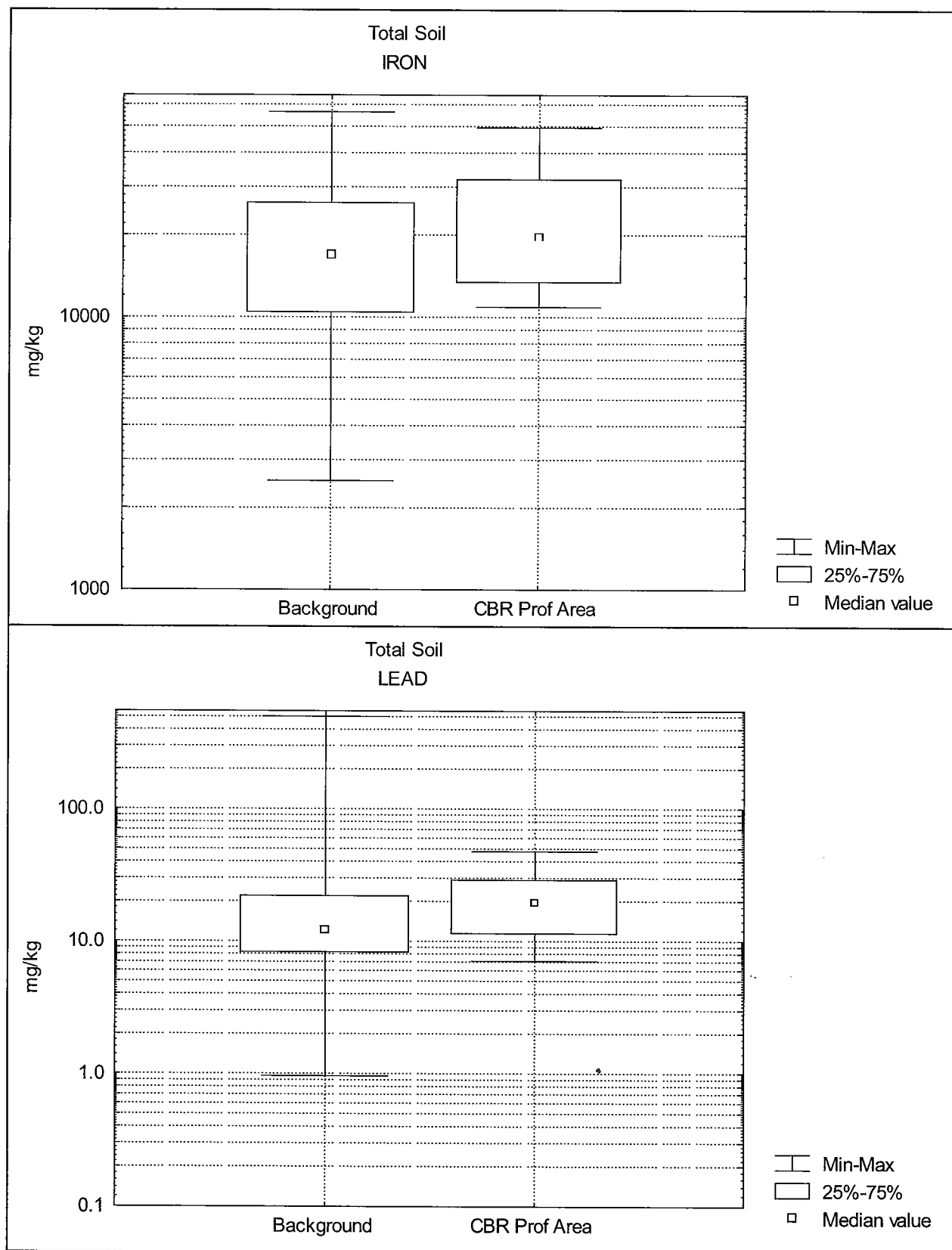


Figure 1-10

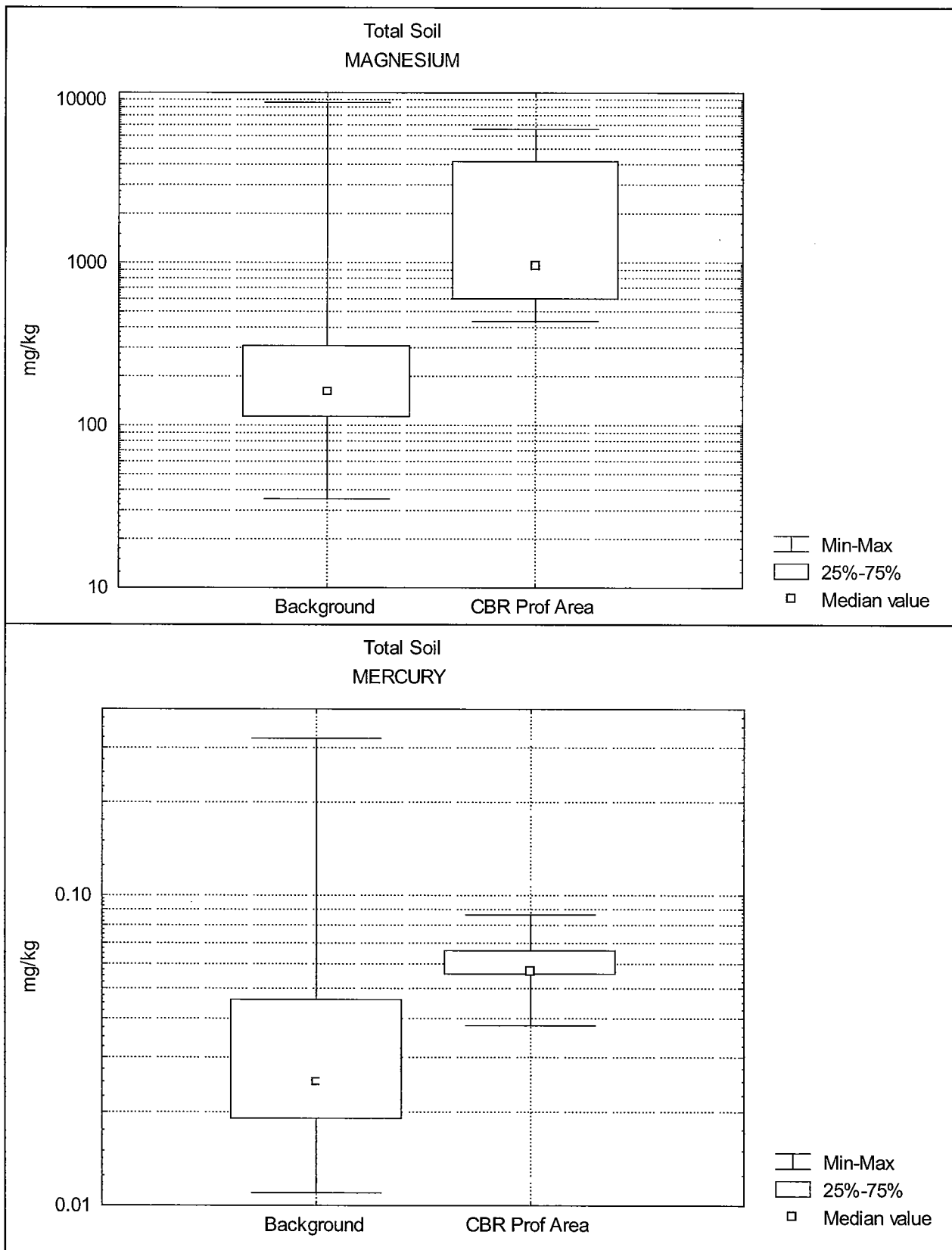


Figure 1-11

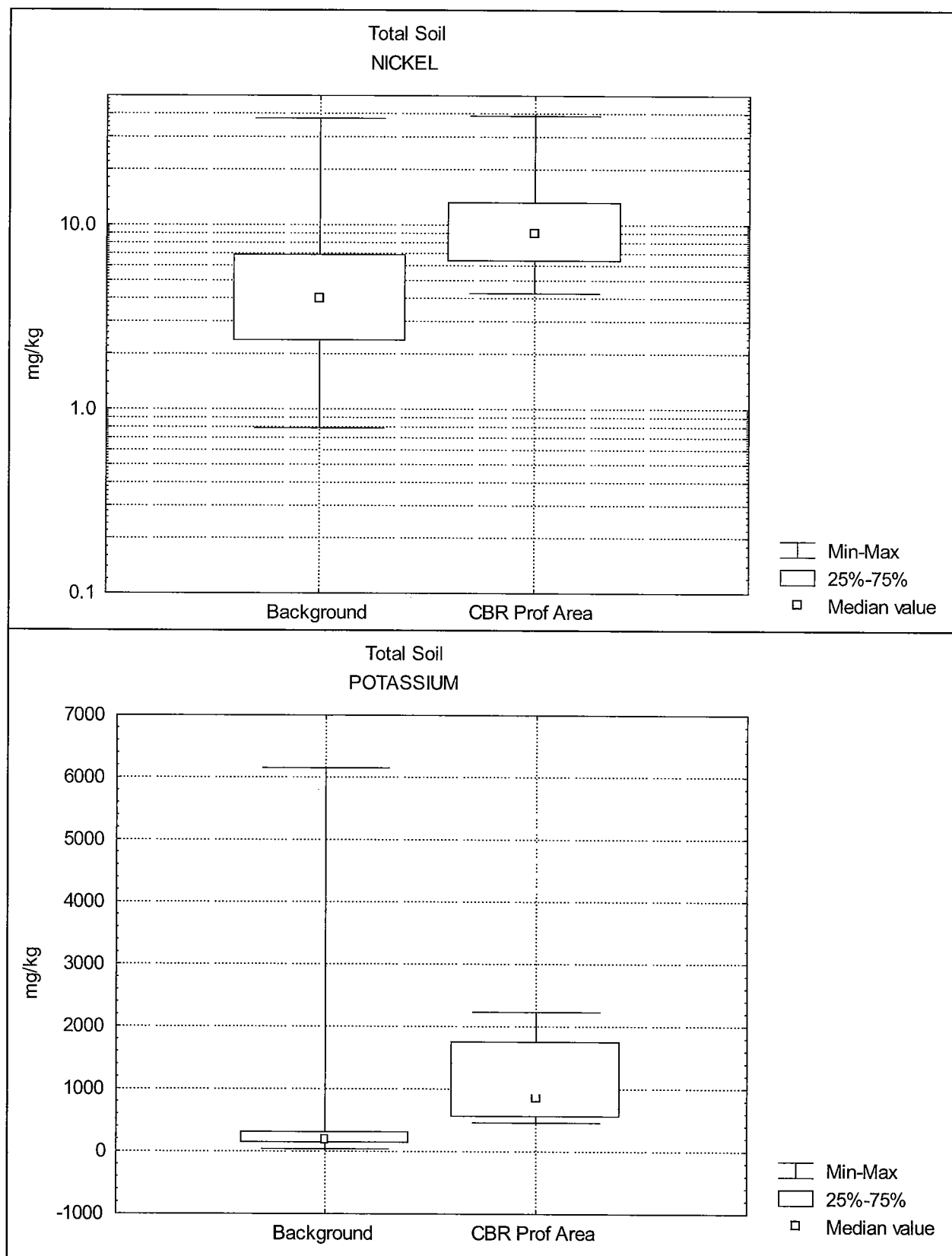


Figure 1-12

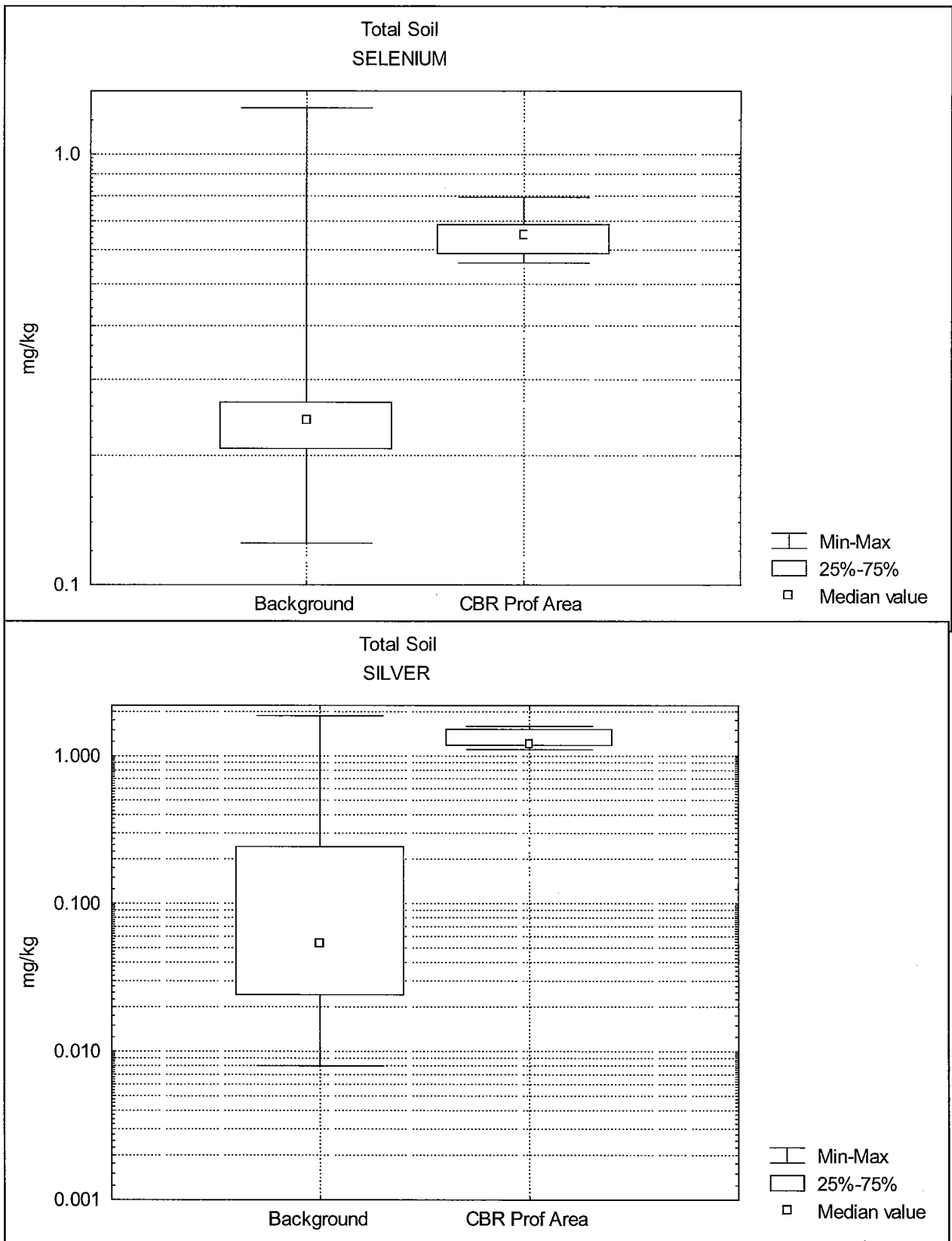


Figure 1-13

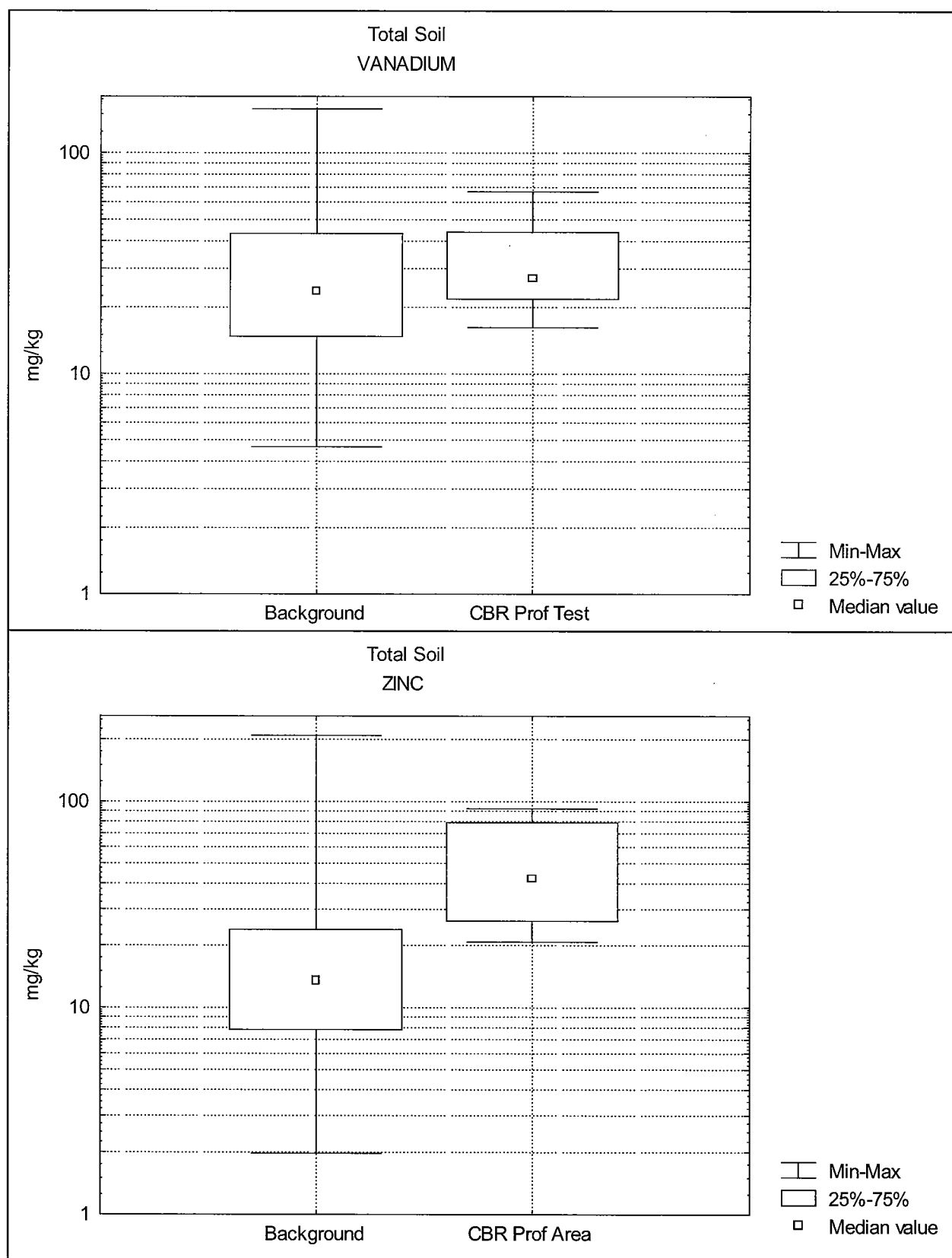


Figure 1-14

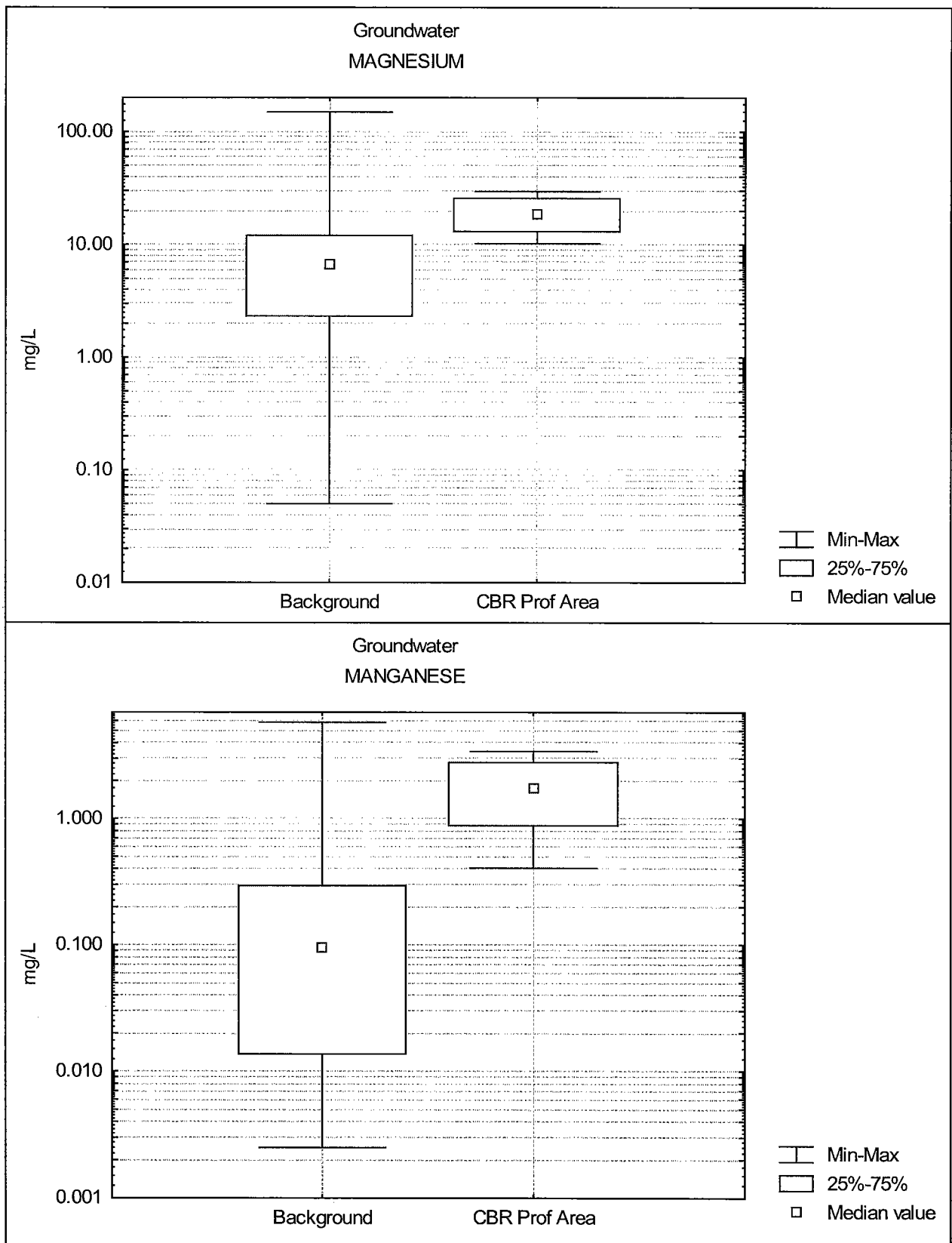
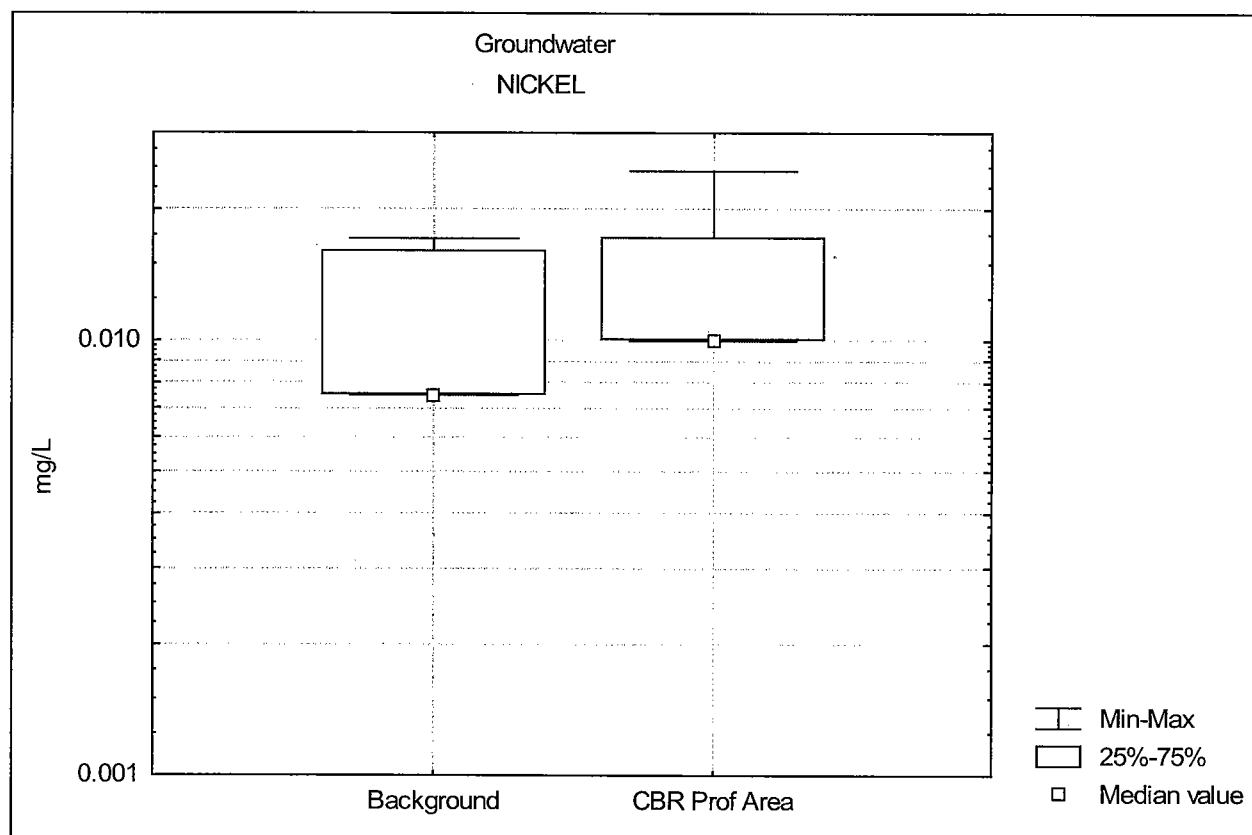




Figure 1-15



## **GEOCHEMICAL**

# **Geochemical Evaluation of Metals in Soil and Groundwater at the CBR Proficiency Area (Parcel 517), Fort McClellan, Alabama**

## **1.0 Introduction**

This report provides the results of a geochemical evaluation of soil and unfiltered groundwater samples from the CBR Proficiency Area (Parcel 517), Fort McClellan, Calhoun County, Alabama. Thirteen elements in total (surface and subsurface) soil and one element in groundwater failed statistical comparison to background. A geochemical evaluation was performed to determine if the elevated concentrations are naturally occurring or if they contain a component of contamination.

Site samples included in the evaluations consist of 7 surface soil samples (obtained from a depth of 0 to 1 foot below ground surface [bgs]) collected in October 2001 and February 2002, 4 subsurface soil samples (obtained from depths of 2 to 3 feet bgs and 7 to 8 feet bgs) collected in October 2001, and 4 unfiltered groundwater samples collected in January 2002. Installation-wide background data for TAL metals in soil, sediment, groundwater, and surface water are provided in the background study report (Science Applications International Corporation, 1998) and are used in the following evaluations.

## **2.0 Geochemical Evaluation Methodology**

If an analyte failed statistical comparison to background, then a geochemical evaluation is performed to determine if the elevated concentrations are caused by natural processes. The importance of geochemical evaluations in distinguishing between site and background data sets has been recognized in the industry (EPA, 1995; Barclift, *et al.*, 2000; U.S. Navy, 2002; Myers and Thorbjornsen, 2004). When properly evaluated, geochemistry can provide mechanistic explanations for apparently high, yet naturally occurring, constituents. Anomalous samples that may represent contamination can also be readily distinguished from uncontaminated samples. This section describes the geochemical evaluation techniques that were employed in the CBR Proficiency Area site-to-background comparisons.

## 2.1 Soil

The geochemical evaluation is based on the natural associations of trace elements with specific minerals in the soil matrix. As an example, arsenic in most uncontaminated oxic soils is almost exclusively associated with iron oxide minerals (Bowell, 1994; Schiff and Weisberg, 1997). (The term “iron oxide” is used here to include oxides, hydroxides, oxyhydroxides, and hydrous oxides of iron.) This association of arsenic with iron oxides is a result of the adsorptive behavior of this particular trace metal in an oxic soil environment. Arsenic is present in oxic soil pore fluid as negatively charged oxyanions ( $\text{HAsO}_4^{-2}$ ,  $\text{H}_2\text{AsO}_4^-$ ) (Brookins, 1988). These anions have strong affinities to adsorb on the surfaces of iron oxides, which maintain a strong positive surface charge (Electric Power Research Institute [EPRI], 1986). If a soil sample has a high percentage of iron oxides, then it is expected to have a proportionally higher concentration of arsenic.

The absolute concentrations of arsenic and iron can vary by several orders of magnitude at a site, but the arsenic/iron ratios in the samples are usually quite constant as long as no contamination is present (Daskalakis and O'Connor, 1995). If a sample has some naturally occurring arsenic plus additional arsenic from an herbicide or some other source, then it will have an anomalously high ratio relative to the other uncontaminated samples. These ratios thus serve as a powerful technique for identifying contaminated samples.

The evaluation includes the generation of plots in which detected arsenic concentrations in a set of samples are plotted on the y-axis, and the corresponding detected iron concentrations are plotted on the x-axis. The slope of a best-fit line through the samples is equal to the average arsenic-to-iron background ratio. If the samples with the highest arsenic concentrations plot on the same linear trend as the other samples, then it is most probable that the elevated concentrations are natural, and are caused by the preferential enrichment of iron oxides in those samples. If the site samples with elevated arsenic concentrations plot above the trend displayed by the uncontaminated samples, then there is evidence that those samples have an excess contribution of arsenic, and contamination may be indicated.

Each trace element is associated with one or more minerals in the soil matrix. Vanadium and selenium, along with arsenic, form anionic species in solution and are associated with iron oxides, which maintain a positive surface charge. Divalent metals such as barium, cadmium, lead, and zinc tend to form cationic species in solution and are attracted to clay mineral surfaces, which maintain a negative surface charge. These trace elements would be evaluated against aluminum, which is a major component of clay minerals. Manganese oxides also have an

affinity to adsorb divalent cations such as barium, cobalt, and lead (Kabata-Pendias, 2001). These trace elements would be evaluated against manganese.

## **2.2 Groundwater**

Elevated concentrations of inorganic constituents in groundwater samples may be due to naturally high dissolved concentrations, the presence of suspended particulates in the samples, reductive dissolution, or contamination resulting from site activities. One primary mechanism that is examined in the Ft. McClellan groundwater site-to-background comparisons is the presence of suspended particulates, as discussed below.

***Effects of Suspended Particulates.*** The presence of trace elements adsorbed on suspended particulates can greatly increase trace element concentrations as reported by an analytical laboratory. These adsorbed trace elements are not in true solution, and can be removed by settling or filtration. The same concepts involved in the evaluation of soil data also apply to groundwater data: samples containing trace elements adsorbed on suspended clay particulates should show a positive correlation with aluminum concentrations, and samples containing trace elements adsorbed on suspended iron oxides should show a positive correlation with iron concentrations. These correlations are evaluated by generating x-y plots of the concentrations of an elevated trace metal versus aluminum or iron (depending on the trace element).

The most common suspended particulates in groundwater samples are clay minerals; hydrous aluminum oxides ( $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ) and hydroxides [ $\text{Al}(\text{OH})_3$ ]; and iron oxide ( $\text{Fe}_2\text{O}_3$ ), iron hydroxide [ $\text{Fe}(\text{OH})_3$ ], and iron oxyhydroxide ( $\text{FeO} \cdot \text{OH}$ ) minerals, collectively referred to as “iron oxides.” All clay minerals contain aluminum and have low solubilities over a neutral pH range of 6 to 8. Measured concentrations of aluminum in excess of ~1 milligram per liter (mg/L) indicate the presence of suspended clay minerals (Hem, 1985; Stumm and Morgan, 1996), with higher aluminum concentrations being a qualitative indicator of the mass of suspended clay minerals. Iron also has a very low solubility under neutral pH and moderate to oxidizing redox conditions, so that measured iron concentrations in excess of ~1 mg/L under these conditions indicate the presence of suspended iron oxides (Hem, 1985).

The presence of suspended clay or iron oxides in groundwater samples has particular importance in the interpretation of trace element concentrations. Most clay particles maintain a negative surface charge under neutral pH conditions, and have a strong tendency to adsorb positively charged (cationic) aqueous species. Iron oxides display the opposite behavior, maintaining a

positive surface charge under neutral pH conditions, and have a strong tendency to adsorb negatively charged (anionic) aqueous species.

Barium, lead, and zinc are usually present in groundwater as divalent cations and thus tend to concentrate on clay surfaces (EPRI, 1984; Brookins, 1988). Arsenic, selenium, and vanadium are usually present under oxidizing conditions as oxyanions, and thus tend to concentrate on iron oxide surfaces (Bowell, 1994; Hem, 1985; Pourbaix, 1974; Brookins, 1988).

Chromium can be present in groundwater as a mixture of aqueous species with different charges, depending on pH (EPRI, 1984). The positive, neutral, and negative charges on these species result in the distribution of chromium on several different types of sorptive surfaces, including clay and iron oxide minerals.

As an example, the concentrations of zinc (y-axis) would be plotted against aluminum (x-axis). If all of the samples display a common linear trend, then it is most likely that the zinc concentrations are due to the presence of suspended clay minerals in the samples. The slope of a best-fit line through the points is equal to the average zinc/aluminum ratio. If some samples plot above the linear trend established by the other samples, then those samples have an anomalously high zinc/aluminum ratio, and most likely contain excess zinc that cannot be explained by these natural processes.

Alternative techniques for assessing the effects of suspended particulates on trace element concentrations are the evaluation of correlations of trace element concentrations versus turbidity, and comparison of analyses of filtered versus unfiltered splits of samples. Turbidity measurements are qualitative, and do not distinguish between suspended clay minerals, iron oxides, and natural organic material, so this approach lacks the resolution provided by trace element versus aluminum or trace element versus iron correlations.

If the concentrations of trace elements in unfiltered samples are correlated with aluminum or iron, then they are most likely adsorbed to the surfaces of suspended particulates. If these correlations are linear, then the elevated concentrations are most likely natural.

### ***3.0 Results of the Geochemical Evaluation for Multiple Elements in Soil***

This section presents the results of the geochemical evaluation of aluminum, barium, beryllium, calcium, copper, lead, magnesium, mercury, nickel, potassium, selenium, silver, and zinc in

surface and subsurface soil samples from the CBR Proficiency Area. Correlation plots are provided in Attachment 1 of this report.

### **Aluminum**

The CBR Proficiency Area soil boring logs note the presence of clays in most of the sampled intervals. Aluminum is a primary component of common soil-forming minerals such as clays, feldspars, and micas. Iron oxides are minerals that are also common in soil. Clays and iron oxides tend to exist as very fine particles, so both aluminum and iron are enriched in samples with finer grain sizes. A plot of aluminum versus iron concentrations can be used to qualitatively assess the relative abundance of these minerals in site soil (Figure 1). The site samples have higher aluminum concentrations than many of the background samples, but they also have proportionally higher iron and lie on the background trend. These observations indicate that aluminum in the site samples is naturally occurring. It is worth noting that iron oxide and clay minerals adsorb specific trace elements (as discussed in Section 2.1), so samples that plot on the upper end of the trend in Figure 1 are expected to contain proportionally higher concentrations of trace elements.

#### Conclusion

Aluminum detected in the site soil samples is naturally occurring.

### **Barium**

Manganese oxides have an affinity to adsorb divalent cations such as barium and cobalt (Kabata-Pendias, 2001). If a soil sample contains a high proportion of manganese oxides, then it is expected to contain high concentrations of manganese and associated trace elements. The site and background samples form a collinear trend in a plot of barium versus manganese (Figure 2). The site samples with the highest barium concentrations also contain the highest manganese concentrations, and lie on the trend established by the other samples. The site subsurface soil samples are shifted slightly higher relative to the site surface soil samples and most of the background samples; however, they all plot on the background trend and are highly correlated ( $R^2 = 0.99$ ). These samples likely reflect the natural (but slight) variability in Ba/Mn ratios in Ft. McClellan soils. Barium detected in the site samples is natural.

#### Conclusion

Barium concentrations detected in the site soil samples are naturally occurring.

### **Beryllium**

Beryllium commonly substitutes for divalent cations, such as magnesium, in minerals (Kabata-Pendias, 2001). A plot of beryllium versus magnesium reveals a common linear trend for the site and background samples (Figure 3). The site samples with the highest beryllium concentrations also contain high magnesium, and lie on the trend established by the other samples. These observations indicate that the elevated beryllium concentrations in the site samples have a natural source.

#### Conclusion

Beryllium detected in the site soil samples is naturally occurring.

## **Calcium**

Calcium and magnesium have similar chemical properties, and magnesium often substitutes for calcium in minerals. A plot of magnesium versus calcium is provided in Figure 4. The background samples exhibit a generally linear trend with a positive slope, and most of the site samples lie on this trend ( $R^2 = 0.64$  and  $0.95$  for the background samples and site surface soil samples, respectively). The site samples with the highest calcium concentrations also have high proportionally higher magnesium, which indicates a natural source for the elevated calcium in the samples.

### Conclusion

Calcium detected in the site soil samples is naturally occurring.

## **Copper**

Copper in soil has an affinity to adsorb on the surfaces of minerals such as clays and iron oxides (Kabata-Pendias, 2001). The background samples form a linear trend with a positive slope in a plot of copper versus iron (Figure 5). The site samples with the highest copper also have proportionally higher iron, and all of the site samples lie on the background trend. This indicates that the copper is associated with iron oxides at ratios consistent with those of the background samples, and is natural.

### Conclusion

Copper concentrations detected in the site soil samples are naturally occurring.

## **Lead**

As discussed in Section 2.1, manganese oxides have an affinity to adsorb divalent cations such as barium, cobalt, and lead (Kabata-Pendias, 2001), so a positive correlation between lead and manganese is expected in uncontaminated soil samples. The background samples form a strong linear trend in a plot of lead versus manganese ( $R^2 = 0.85$ ) (Figure 6). The site samples exhibit similarly strong correlations ( $R^2 = 0.91$  and  $0.99$  for the surface and subsurface intervals, respectively), and all lie on the background trend. These observations indicate that lead in the site samples is associated with manganese oxides at a nearly constant ratio, and is natural.

### Conclusion

Lead concentrations detected in the site soil samples are naturally occurring.

## **Magnesium**

Magnesium is a common component of minerals such as clays and micas, which contain aluminum as a primary constituent. A plot of magnesium versus aluminum reveals a generally linear trend for the background samples (Figure 7). The site samples all lie on the background trend, indicating that the magnesium is associated with aluminum-bearing minerals at ratios consistent with those of the background samples, and is natural.

### Conclusion

Magnesium detected in the site soil samples is naturally occurring.



## **Mercury**

Mercury concentrations in soil are commonly controlled through organic complex formation (Kabata-Pendias, 2001), so poor correlations between mercury and the primary reference elements (aluminum, iron, manganese) are often observed, even in uncontaminated soil samples. Mercury shows poor correlations versus the reference elements in the background samples, but is well correlated with manganese in the site samples ( $R^2 = 0.84$  for the site surface soil interval) (Figure 8). The site samples exhibit Hg/Mn ratios similar to those of the background samples, and they all lie on the general background trend. The site sample with the highest mercury concentration also exhibits the highest manganese concentration. These observations suggest that mercury detected in the site samples is naturally occurring.

### Conclusion

Mercury concentrations detected in the site soil samples are naturally occurring.

## **Nickel**

Nickel is commonly associated with iron oxides (Kabata-Pendias, 2001). If a soil sample contains a high proportion of iron oxides, then it is expected to contain high concentrations of iron and associated trace elements such as nickel. A plot of nickel versus iron reveals a generally linear trend with a positive slope for the background samples, and all of the site samples lie on this general background trend (Figure 9). Nickel in the site samples is associated with iron oxides at ratios consistent with those of the background samples, and is natural.

### Conclusion

Nickel in the site soil samples is naturally occurring.

## **Potassium**

Potassium is a major element that is a common constituent of minerals such as clays, which also contain aluminum. The site and background samples form a common linear trend in a plot of potassium versus aluminum (Figure 10). The site samples with the highest potassium also have proportionally higher aluminum, and lie on the linear trend. This indicates that these samples are preferentially enriched in clays (and other aluminum-bearing minerals) and that the potassium is natural.

### Conclusion

Potassium detected in the site soil samples is naturally occurring.

## **Selenium**

Evaluation is hindered because of the high percentages of nondetects in both the site and background data sets, and there are poor correlations observed between selenium and the primary reference elements (aluminum, iron, and manganese) in the site samples. The three detected concentrations in the site samples are estimated values below the reporting limit, and range from 0.65 J to 0.757 J mg/kg. There is a high degree of uncertainty surrounding such estimated values, which may explain the poor correlations. However, all of the site detections are below the background maximum of 1.28 mg/kg, so any contamination, if present, would not be significant.

### Conclusion

Selenium concentrations detected in the site soil samples are most likely naturally occurring.

### **Silver**

A plot of silver versus aluminum is provided in Figure 11. The two site samples with detectable silver have higher concentrations most of the background samples, but they also have the highest aluminum concentrations. This suggests that these two site samples are preferentially enriched in clay minerals and associated trace elements, and that the silver is natural. It is important to note that both site detections are estimated values (1.53 J and 1.57 J mg/kg) below the reporting limit, and that such values are highly uncertain. In comparison, the background detections are mostly unestimated concentrations ranging from 0.019 to 1.87 mg/kg, with a mean of 0.128 mg/kg (14 of the 82 background samples are estimated values). Additionally, the site samples are characterized by higher reporting limits relative to the background samples: the site reporting limits range from 2.21 to 3.18 mg/kg, with a mean of 2.50 mg/kg, whereas the reporting limits for the background nondetects range from 0.016 to 1.2 mg/kg, with a mean of 0.293 mg/kg [reporting limit data are unavailable for the background detected concentrations]. The uncertainty associated with the estimated site concentrations, combined with the difference in reporting limits between the data sets, may explain why the site samples do not exhibit the same Ag/Al ratios exhibited by the background samples.

### Conclusion

Elevated silver concentrations are observed in soil samples with high aluminum, and are natural.

### **Zinc**

Zinc commonly substitutes for magnesium in silicate minerals (Kabata-Pendias, 2001), so a positive correlation between zinc and magnesium concentrations is often observed for uncontaminated soil samples. The site and background samples form a common linear trend in a plot of zinc versus magnesium ( $R^2 = 0.66$  and  $0.96$  for the site surface and subsurface intervals, respectively) (Figure 12). The samples with high zinc also contain high magnesium, and lie on the background trend. These observations indicate that zinc in the site samples is associated with magnesium-bearing minerals at a relatively constant ratio, and is natural.

### Conclusion

Zinc detected in the site soil samples is naturally occurring.

## ***4.0 Results of the Geochemical Evaluation for Magnesium in Groundwater***

This section presents the results of the geochemical evaluation of magnesium in unfiltered groundwater samples from the CBR Proficiency Area. Correlation plots are provided in Attachment 1.

Field-measured pH readings for the site groundwater samples range from 6.00 to 6.49 standard units (mean of 6.35), indicating generally neutral-pH groundwater conditions at the sample

locations. Field-measured dissolved oxygen readings range from 1.06 to 7.17 mg/L, with a mean of 4.42 mg/L, and oxidation-reduction potential readings range from -83 to +307 millivolts (mV), with a mean of +57 mV. These readings suggest oxidizing to mildly reducing conditions at the sample locations.

## **Magnesium**

Magnesium and calcium are both major dissolved constituents in groundwater, and are derived from the weathering of silicate and carbonate minerals. A plot of magnesium versus calcium reveals a strong linear trend with a positive slope for the background samples ( $R^2 = 0.91$ ) (Figure 13). The site samples all have moderately high magnesium, but they also have proportionally higher calcium and lie on the linear background trend. Magnesium in these samples is natural.

## Conclusion

Magnesium concentrations in the site groundwater samples are naturally occurring.

## **5.0 Summary**

This section summarizes the results of the geochemical evaluations of selected inorganics in soil and groundwater samples from the CBR Proficiency Area (Parcel 517).

**Soil.** Geochemical evaluation indicates that all of the aluminum, barium, beryllium, calcium, copper, lead, magnesium, mercury, nickel, potassium, selenium, silver, and zinc concentrations detected in the surface soil samples are naturally occurring. The available data do not indicate contamination for these elements in the site soil samples.

**Groundwater.** Geochemical evaluation indicates that magnesium in the site samples is naturally occurring. All of the other elements detected in the site samples passed statistical comparison to background, and did not require geochemical evaluation.

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## **ATTACHMENT 1**

